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ORGANIC REAGENTS FOR METALS

'ANALAR' STANDARDS

FOR LABORATORY CHEMICALS

3rd Edition in Press

With a Foreword by the late

PROFESSOR JOCELYN F. THORPE
C.B.E., Ph.D., D.Sc., F.R.S.
One time Professor of Organic Chemistry in the University of London
(Imperial College)

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ORGANIC REAGENTS FOR METALS

AND FOR CERTAIN ACID RADICALS

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RESEARCH LABORATORY OF
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FOREWORD

BY

A. D. MITCHELL, D.Sc., F.I.C.,
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AND

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Principal, County Technical College, Guildford

It is fortunate for analysts that under present conditions Messrs. Hopkin & Williams should be in a position to produce a fourth edition of this very useful book, in which 43 reagents are dealt with and reference is made to more than 1300 publications. The interest shown in this subject during the past decade may be roughly measured by a comparison with the first edition (1933), which contained descriptions of 17 reagents and less than 200 references.

All the information has been brought thoroughly up to date, and the enlarged bibliographies, which are a valuable feature, include references to papers which have been published in the current year. Critical and constructive comments by the firm's own research staff occur throughout the book and bear testimony to the thoroughness of the revision, and the various notes on the keeping qualities of reagent solutions will save both time and worry.

The extension of the section on that protean reagent ' oxine ' will be appreciated, and other noteworthy features are the change from ' c.c.' to ' ml.' and a differentiation between ' selective ' and ' specific ' in accordance with recent (and belated!) convention in describing the properties and scope of reagents.

The compilers are also to be congratulated on their care in avoiding ambiguity as to concentrations of reagents which are normally available in solution, such as ammonia and nitric and hydrochloric acids. The analyst using this book will not have to speculate as to what is meant by, for example, ' 10 per cent. HCl '—whether actual HCl or concentrated (11N) acid, and, if the latter, whether by weight or by volume—for this frequent cause of annoyance is eliminated by precise statement.

This edition maintains the high standard of its predecessors, and it is gratifying that such a wide range of products is available from its sponsors at a time when rapid methods of analysis are of great national importance.

A. D. MITCHELL.
A. M. WARD.

May, 1943

PREFACE TO FOURTH EDITION

APART from general revision and amplification of existing monographs we have included for the first time $\alpha\alpha'$-dipyridyl, fluorescein, α-furil dioxime, 9-methyl-2 : 3 : 7-trihydroxy-6-fluorone and *p*-nitrobenzene-azo-orcinol. Two other reagents, α-dinitrodiphenylamine sulphoxide and sodium dihydroxytartrate osazone, do not appear to have met with sufficient interest to justify their inclusion in the present edition. Nevertheless these substances are still obtainable from the company.

The more noteworthy points of revision have received comment in a new foreword for which we are indebted to Drs. A. D. Mitchell and A. M. Ward.

The chief function remaining to this preface is the expression of acknowledgments, first to Drs. Mitchell and Ward for their interest and valuable suggestions. Their own publication, *Modern Methods in Qualitative Chemical Analysis*, has also been a valuable source of reference. We have also drawn extensively upon Dr. Schoeller's *The Analytical Chemistry of Tantalum and Niobium.*

My colleagues and collaborators, Dr. R. J. Shennan, M.Sc., A.I.C., and Mr. R. A. Reed, B.Sc., F.I.C., and myself also acknowledge the work of my previous collaborators, Dr. J. G. Jackson, M.Sc., A.I.C., and Dr. A. J. Lindsey, M.Sc., F.I.C.

W. C. JOHNSON,
Chief Chemist.

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PREFACE TO FIRST EDITION

THE following pages have been prepared in response to requests from a number of our customers for information on the use of the many organic reagents which, during recent years, have assumed considerable importance in analytical work but which in many instances have not yet found their way into standard text books.

It has been our object to include only such reagents as are likely to prove of real utility and to offer advantages over the already existing methods, but it is not claimed that the work is by any means exhaustive either in respect of the number of compounds described or in respect of the information given on any particular compound. We have rather chosen the most important reagents and have described their most important applications. Information on special applications, where it is available, may be traced by reference to the bibliographies, which we have endeavoured to make comprehensive.

To satisfy ourselves on the claims of each reagent for inclusion, we have carried out analyses employing the substances, and have checked in the laboratory almost all the matter which appears in the text of this volume. In certain cases details of manipulation here recommended differ from those described in the literature. Such modifications are the result of our own practical experience, in which we have found the technique of the literature unreliable or faulty.

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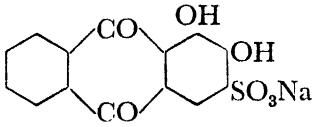
ALIZARIN RED S

(Sodium alizarin sulphonate)



Mol. Wt. 342

Reagent for Fluoride, Aluminium, Zirconium and Scandium

Alizarin red S, a water soluble yellow dyestuff, gives a pink coloration with an ammoniacal solution of an aluminium salt which is not discharged on acidification with dilute acetic acid.

The reagent is used as a filtered 0·1 per cent. aqueous solution.

Detection of Aluminium

To the slightly acid test solution are added five drops of reagent solution followed by a slight excess of 5N ammonia, and a further excess of 5N acetic acid.

Under these conditions, one part of aluminium in 5,000,000 parts of solution gives a positive test, and aluminium may be detected in presence of at least 1000 times as much magnesium, beryllium, thallium, barium, strontium, calcium, zinc, cadmium, nickel, mercury, silver, manganese, and lead.

In ammoniacal solution with potassium cyanide the same excess of copper does not interfere.

In presence of arsenic, antimony, and bismuth the test is performed in presence of sodium citrate without interference.

Tin, cobalt, iron, and chromium interfere and should be separated.

Determination of Aluminium

The neutral solution under test (5 to 20 ml.) is acidified with 1 ml. 5N hydrochloric acid, 10 ml. glycerol added, followed by 5 ml. reagent solution, and the volume diluted to 40 ml. with water. After the addition of 2 ml. 5N ammonia, stand for five minutes, acidify with 5 ml. 5N acetic acid, and compare with standards made up simultaneously and containing from 0·005 to 0·05 mg. Al.

Should the aluminium concentration be too high it is diluted accurately so as to fall within the standard range.

Detection of Zirconium

Zirconium salts give a red colour with the reagent that persists on acidification with hydrochloric acid.

Three drops of reagent solution are added to 50 ml. of the hydrochloric acid test solution, any red colour produced indicating zirconium. The test will detect zirconium in a concentration of one part in 2,500,000 parts of solution.

A positive test is given in presence of at least 1000 times as much zinc, aluminium, magnesium, cadmium, mercury, lead, silver (in nitric acid), tin, beryllium, calcium, barium, strontium, iron, copper, arsenic, antimony, bismuth, nickel, and manganese.

Cobalt interferes as do fluorides, sulphates, phosphates, tungstates and molybdates.

Detection and Determination of Fluoride

The acid zirconium lake is decolorised by fluorides and silicofluorides to an extent proportional to the concentration of fluorine present.

When used as a test for combined fluorine, one part in 5,000,000 parts of solution may be detected.

For determining the fluoride content of water samples, an approximate titration is first carried out on 20 ml. of sample, or an aliquot portion diluted to 20 ml.

This is followed by a more accurate colorimetric procedure.

The indicator both for titration and the subsequent colorimetric estimation is made by mixing solutions A and B in the proportions 3 : 2 by volume, and diluting the mixture ten times with water.

Solution A: 0·4 per cent. zirconium nitrate aqueous solution.
Solution B: Shake 1 g. alizarin red S with 100 ml. ethyl alcohol, filter and dilute to 250 ml. with more alcohol.

A M/200 solution of thorium nitrate is prepared by dissolving 2·4 g. anhydrous thorium nitrate in 1 litre water and standardising on N/50 sodium fluoride (0·84 g. NaF per litre) by the same procedure as described below for determinations.

To 2 ml. of test solution is added 1·5 ml. indicator solution, followed by 25 ml. neutral glycerol. Should the colour of the zirconium lake persist, it is just decolorised by the addition of N/5 hydrochloric acid. The solution is now titrated with the standard N/50 thorium nitrate to faint reappearance of colour; the fluoride is precipitated as thorium fluoride.

A sharp end-point, however, is not obtained and only an approximate fluorine content may be determined by this procedure.

For the more accurate colorimetric method, a portion of the original test solution is diluted, if necessary, to give a fluorine content of approximately one part in 2,000,000 parts of solution. A series of standards is now made containing from 0·2 to 1·2 ppm. F in steps of 0·2 ppm.

To these and the test solution (volume 50 ml.) are added 2 ml. hydrochloric acid (S.G. 1·18) and 1 ml. 10 per cent. sodium nitrite solution (to remove free chlorine), followed by 1·5 ml. indicator solution. After standing for fifteen minutes the fluorine content may be estimated accurately to 0·2 ppm.

In the analysis of commercial samples, the fluorine is usually distilled as fluosilicic acid under various conditions, the distillate made alkaline and evaporated to low bulk.

Hoskins and Ferris [24] state that the pH before titration is very important and that it should be maintained by the use of a chloroacetic acid buffer.

Armstrong [18] prefers a modification of this technique, using no zirconium in the indicator.

Another notable modification is that of Ugnyachev and Bilenko [35], who titrate fluoride in strongly acid solution at 0° with 2 per cent. zirconium nitrate using an aqueous solution of alizarin red S as indicator.

Detection of Scandium

The reagent gives a violet precipitate with scandium salts, which is insoluble in 10 per cent. acetic acid (separation from other rare earth metals). Thorium is also precipitated under these conditions.

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ALLYL IODIDE HEXAMINE

$[(CH_2)_6N_4]\ [CH_2 : CH \cdot CH_2I]$

Mol. Wt. 308·2

Reagent for Cadmium

Allyl iodide hexamine is a compound of hexamethylene tetramine and allyl iodide. It is a white crystalline substance which has no definite melting-point but which sinters at 158° and decomposes at about 170°. The substance is soluble in water and alcohol and has been used for the detection and determination of cadmium. It is, however, not so sensitive as either β-naphthoquinoline or phenyltrimethylammonium iodide, and has not been successfully developed for quantitative work. Low and inconsistent results were obtained [3, 4, 5].

When an aqueous solution of allyl iodide hexamine is added to a neutral solution of a cadmium salt a white crystalline precipitate is produced. The complex has the composition $CdI_2 2[C_9H_{17}N_4I]$ and contains 11·44 per cent. of cadmium. It is soluble in acids and alkalis and salts of the alkali metals.

Detection of Cadmium

To the neutral solution under test an equal volume of a 5 per cent. aqueous allyl iodide hexamine solution is added. A white precipitate or turbidity is produced in the presence of cadmium, one part of which can be detected in 15,000 parts of water by this reaction.

Metals which give precipitates with soluble iodides interfere (Cu, Pb, Ag, Sb, Hg and Bi).

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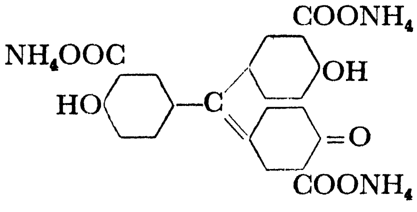
AMMONIUM AURINE TRICARBOXYLATE

‘ Aluminon ’



Mol. Wt. 473·4

Reagent for Aluminium

The ammonium salt of aurine tricarboxylic acid is a dye capable of forming brilliantly coloured lakes with several metals. The substance itself is a brownish red powder freely soluble in water. Under suitable conditions the compound forms a bright red lake with aluminium, and has therefore been found of considerable use in the detection of small quantities of this metal and in its colorimetric estimation.

The aluminium lake is first formed in an acetate buffer mixture, and the solution subsequently made alkaline with ammonia and ammonium carbonate. Chromium forms a similar lake in acetate solution, but this is rapidly decomposed after addition of ammonia and ammonium carbonate. Iron behaves similarly to aluminium and should be removed. Beryllium also gives a lake similar to that formed by aluminium. Phosphate if present in any considerable quantity prevents formation of the aluminium lake. In such a case aluminium phosphate may be precipitated by addition of ammonia. The precipitate, which contains a sufficiently low proportion of phosphate, may be redissolved in acid and tested by the usual method. Under the conditions of the method described below, silicates and salts of bismuth, lead, antimony, tin and mercury give white precipitates. Calcium and barium are also precipitated, if present, on addition of the carbonate solution. Cadmium, zinc, cobalt and nickel have no disturbing effect unless the two last-named metals are present in quantity sufficient to impart their characteristic colours to the ammoniacal solution.

Detection of Aluminium

Solutions required:

(1) Hydrochloric acid N/1.
(2) Ammonium acetate solution 25 per cent. *w/v*.
(3) Ammonium salt of aurine tricarboxylic acid 0·1 per cent. in water.

(4)		
	Ammonium carbonate - - -	16 g.
	Ammonia 5N - - - -	20 ml.
	Water - - - - -	80 ml.

The solution to be tested is rendered free from iron, evaporated to a bulk of about 5 ml., adjusted to near neutrality, and 5 ml. of N/1 hydrochloric added; or the precipitate obtained by addition of ammonia filtered off and redissolved in 5 ml. of N/1 hydrochloric acid. Five ml. of ammonium acetate and 5 ml. of the reagent solution are now added, and the test allowed to stand five minutes to allow formation of the lake, the solution becoming red in the presence of traces of aluminium, a red precipitate forming in presence of larger quantities. On the addition of 10 ml. of ammonium carbonate solution the colour becomes less intense, but with quantities of aluminium down to 0·02 mg. a definite red coloration persists.

A higher degree of sensitivity may be obtained if ammonium carbonate is added in smaller quantity than is specified above. Thus, by adjusting conditions so that the final pH of the solution does not exceed 7·3, Winter and his co-workers [9] were able to estimate quantities of aluminium down to 0·005 mg. Roller [15] formed the lake in a solution buffered at pH 6·3 with ammonium acetate and hydrochloric acid and made no subsequent addition of ammonia or carbonate since, at this hydrogen ion concentration, any excess dye is of a neutral orange tint. A sensitivity of 0·0001 mg. Al is claimed for this technique, but we have not obtained definite reactions for quantities less than 0·0005 mg. The interference of chromium is not eliminated, but the method has the advantage that calcium is not precipitated.

Some disagreement exists in the literature as to the necessity of a final excess of ammonium carbonate. Certain metals give lakes which are said to be decolorised only on addition of carbonate [3, 4]. The alternative methods are therefore both mentioned above, and circumstances must direct the choice of the user.

Colorimetric Determination of Aluminium

The reagent has been successfully applied to the colorimetric estimation of aluminium in water, foodstuffs and other organic materials. The methods described above may be employed for approximate colorimetric purposes using Nessler glasses and standards prepared simultaneously from a standard aluminium solution. Some minutes are required, as already indicated, for the full development of the lake, which, after addition of the ammonia and carbonate, gradually fades. It is evident, therefore, that strict standardisation of conditions is essential. For accurate work the reader is advised to adopt one of the rather more refined methods detailed in the literature [5, 7, 9, 14, 15].

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AMMONIUM NITROSOPHENYLHYDROXYLAMINE

'Cupferron'

$C_6H_5{\cdot}N(NO){\cdot}ONH_4$

Mol. Wt. 155·15

Reagent for Iron, Titanium, Zirconium and other metals

The ammonium salt of nitrosophenylhydroxylamine is a white or buff coloured crystalline compound readily soluble in water. The solid compound shows a tendency to become more deeply coloured through decomposition on long storage and it is usually recommended to place in the stock bottle a piece of ammonium carbonate, which has the effect of delaying decomposition. The substance usually forms a slightly turbid solution in water, but filtration provides a solution quite suitable for use. The 5 per cent. aqueous solution which is usually employed becomes dark with the passage of time but may safely be used after several days.

By replacement of the ammonium radical, cupferron forms insoluble compounds with a number of metals, and methods have been evolved for the estimation of copper, iron, titanium, zirconium, vanadium, thorium, tin, aluminium, bismuth, mercury and gallium.

The salts of Fe, Cu, Zr, Th, Nb, Ta, V and Sn are soluble in ether, the Fe salt being very soluble, thus providing a convenient method for the rapid separation of iron, as, for example, in the determination of lead by dithizone.

As a reagent for copper, cupferron possesses no particular advantages, since silver, lead, mercury, tin, bismuth and iron are either partially or completely precipitated under the same conditions as are required for the precipitation of copper.

Iron, titanium and zirconium are precipitated from strongly acid solution by means of cupferron, and may thus be easily separated from aluminium, chromium, manganese, nickel, cobalt, zinc, alkaline earth metals, magnesium and alkali metals, none of which is precipitated under these conditions. Gallium is also precipitated from dilute sulphuric acid, thus providing a method for its separation from indium.

Since the use of the reagent in acid solution would appear to be the application of widest interest, the methods for iron, titanium and zirconium are detailed below, the reader being referred to the original literature for other estimations and separations.

Determination of Iron

The solution containing about 0·1 g. of ferric iron in 150–200 ml. is rendered strongly acid with hydrochloric acid, and, in the cold, a 5 per cent. solution of cupferron is added until further addition produces in the liquid a white precipitate of nitrosophenylhydroxylamine as distinct from the brownish red colour of the iron compound. The addition is made slowly down the side of the beaker and vigorous stirring is maintained to produce a precipitate as granular as possible, though it will usually be found that the iron compound takes a somewhat tarry form. Heating is to be avoided since the reagent is decomposed rapidly in hot acid solution.

Filtration is not to be long delayed since it is reported [7] that the precipitated metallic complexes are only stable in presence of excess of the reagent and, even in cold acid, the excess reagent gradually decomposes. The precipitate is filtered off in an ashless filter paper and washed several times with dilute hydrochloric or sulphuric acid containing a few drops of the reagent solution, then with 5N ammonia solution to remove excess of cupferron and to convert the iron compound into ferric hydroxide. This conversion renders the final ignition less tedious and lessens risk of reduction of the ferric oxide by the burning organic matter. The precipitate is ignited with the filter paper, gently at first, until all the organic matter is destroyed, and then strongly. The iron is finally weighed as Fe_2O_3.

$$\text{Wt. of } Fe_2O_3 \times 0{\cdot}699 = \text{Wt. of Fe.}$$

The above method separates iron from aluminium, chromium, manganese, nickel, cobalt, zinc, alkaline earth metals, magnesium and alkali metals. When copper is present it has been recommended to adopt the same procedure since the copper compound is soluble in ammonia and is thus removed in the washing operation. It seems preferable, however, to remove all metals which are precipitated by hydrogen sulphide in acid solution by the ordinary method, previous to treatment with cupferron.

Determination of Titanium

The solution containing about 0·05 g. of tetravalent titanium in 150–200 ml. is made strongly acid and a 5 per cent. solution of cupferron added down the side of the beaker with vigorous stirring. The titanium-cupferron compound is yellow, and after allowing the precipitate a few minutes to settle the supernatant liquid is tested with a few drops of the reagent, excess of cupferron being shown by the appearance of a white crystalline precipitate. The precipitate is filtered on an ashless paper and washed thoroughly with dilute hydrochloric acid containing a little cupferron. The precipitate is ignited gently until all the organic matter is consumed, then strongly, and weighed as TiO_2.

$$\text{Wt. of precipitate} \times 0{\cdot}600 = \text{Wt. of Ti.}$$

The above method affords a separation of titanium from aluminium, chromium, manganese, nickel, cobalt, zinc, alkaline earth metals, magnesium, and alkali metals. Iron may conveniently be removed by reduction with hydrogen sulphide and precipitation with ammonia in tartrate solution by the method of Thornton [12, 13].

Zirconium is estimated by the same method as is described for titanium.

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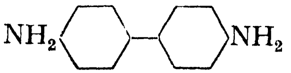
BENZIDINE



Mol. Wt. 184·2

Reagent for Sulphate and Tungstate

Benzidine, a buff-coloured solid, melting at 128°, forms an insoluble sulphate and tungstate, enabling estimation of both ions to be made.

Determination of Sulphate

The reagent is prepared by shaking 8 g. benzidine hydrochloride with 1 litre of water and filtering. This reagent should be prepared weekly.

To the slightly acid test solution the reagent solution is added until precipitation appears complete and a slight excess is present in the supernatant liquid to the extent of at least 1 g. benzidine per litre. The optimum pH for precipitation has been found to be 2·6–3·0.

After a few minutes place the whole in iced water for fifteen to thirty minutes. The precipitate is filtered in a macrodetermination, and centrifuged at 3000 r.p.m. for five to thirty minutes in a microdetermination. The precipitate is washed with 80 per cent. alcohol and then evaluated by one of several methods. The benzidine sulphate may be determined by titration in hot suspension with dilute alkali, or by titration with dilute barium chloride using sodium rhodizonate as indicator.

Alternatively the benzidine may be determined by diazotisation followed by coupling in alkaline solution with phenol or thymol. Another method is to treat the precipitate with acidified hydrogen peroxide and ferric chloride, comparing the colour given with standards.

Finally the benzidine may be evaluated by titration with permanganate.

Methods have been described for the determination of sulphate in blood, urine, sera and soil extracts.

Determination of Tungstate

The reagent for this purpose is prepared as a 2 per cent. solution of benzidine in 1 per cent. hydrochloric acid (1 per cent. *w/v* HCl).

The neutral tungstate solution containing approximately 0·3 g. WO_3 in 200 ml., is acidified with 1 ml. of N/1 sulphuric acid and heated.

To the boiling solution is added 30 ml. reagent solution, and after standing to allow the mixed precipitate of tungstate and sulphate to settle, it is filtered at the pump. After washing with a solution containing 3 per cent of the original reagent solution, the precipitate is dried and ignited to WO_3.

Other Uses

A number of metals, when exerting their maximum valency, give blue colours with the reagent, used as a 0·05 per cent. solution in 10 per cent. acetic acid.

It has been used in this way for the detection of lead, cerium, thallium, manganese, chromium and gold. Manganese has also been estimated by the reagent used in nitric acid solution.

Addition of dimethylglyoxime to a cobalt solution followed by benzidine or *o*-tolidine gives a brown colour [46].

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α-BENZOIN OXIME

'Cupron'

$$C_6H_5 \cdot CH(OH) \cdot C(:NOH) \cdot C_6H_5$$

Mol. Wt. 227·25

Reagent for Molybdenum and Copper

α-Benzoin oxime is a white crystalline powder, melting at 152°, very sparingly soluble in water, and fairly soluble in alcohol. The oxime of benzoin can exist in two stereoisomeric forms, known as the α- form, melting at 152°, and the β- form, melting at 99° [3].

The α- form only is employed as a reagent; in what follows, the prefix α- is omitted, and it is to be understood that the α- form alone is used.

The reagent is employed as a 1 per cent. solution in alcohol. An acetone solution of benzoin oxime is unsuitable as a reagent as it decomposes on standing [17].

Employment in Alkaline Solution

When an alcoholic solution of benzoin oxime is added to an ammoniacal solution of a copper salt, a green precipitate is produced. The precipitate is insoluble in water, alcohol, dilute ammonia, acetic and tartaric acids; soluble in dilute mineral acids, and slightly soluble in concentrated ammonia. Its composition corresponds to the formula $(C_{14}H_{11}O_2N)Cu$. When the reaction is carried out in simple ammoniacal solution, cadmium and zinc give no precipitate, but cobalt and nickel, contrary to the statement of Feigl [1], do furnish precipitates, of brownish and buff colour respectively. If, however, the reaction is carried out in ammoniacal solution containing tartrate ions, copper is still quantitatively precipitated whilst cobalt and nickel furnish no precipitate. Under these conditions, lead, iron, and aluminium also give no precipitate, and the reagent is therefore specific for copper in ammoniacal tartrate solution.

Employment in Acid Solution [8]

In mineral acid solution, benzoin oxime furnishes precipitates with the following: molybdenum, tungsten, palladium, chromium (vi), vanadium (v), and tantalum.

Niobium and silicon interfere somewhat, and should be removed before the determination of any of the above elements.

The following are not precipitated: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, aluminium, iron, titanium, zirconium, chromium (iii), vanadium (iv), cerium, uranium, nickel, cobalt, manganese, zinc, selenium, tellurium, rhenium, ruthenium, rhodium, osmium, indium, and platinum.

Detection of Molybdenum

Twenty ml. of the solution to be tested are acidified with sulphuric acid, and 1 ml. of the reagent added. In concentrations of molybdenum greater than one in 200,000 a white turbidity or precipitate is at once produced, whilst with a concentration of one in 500,000 a turbidity is visible after one hour.

Determination of Molybdenum

The following technique is taken from the paper cited under [8]. The solution should contain not more than 0·15 g. of hexavalent molybdenum in a volume of 200 ml., which should be acidified by the addition of 10 ml. of sulphuric acid (sp. gr. 1·84). If vanadates or chromates are present, sufficient freshly-prepared solution of sulphurous acid to ensure their reduction is added, after which the solution is boiled. It is then cooled to 5°–10° and, with stirring, 10 ml. of a 2 per cent. alcoholic solution of benzoin oxime, plus 5 ml. extra for each 0·01 g. of molybdenum present, are slowly added. With continued stirring, sufficient bromine water to tint the solution a pale yellow, followed by a further 5 ml. of the reagent are added. The solution is allowed to remain at 5°–10° for a further fifteen minutes with occasional stirring, a little filter-paper pulp added, then filtered through a paper of close texture. The precipitate is washed with 200 ml. of a cold, freshly prepared solution containing 25–50 ml. of the reagent (2 per cent. solution in alcohol) and 10 ml. of sulphuric acid (sp. gr. 1·84) per litre. On standing, the filtrate will deposit needlelike crystals if sufficient reagent has been employed. The washed precipitate is transferred to a platinum crucible, slowly charred over a very low flame, then ignited to constant weight at about 500°. The product is MoO_3

Alternatively the molybdenum trioxide may be dissolved in ammonia or in caustic soda solution and estimated either as lead molybdate [19] or by a volumetric procedure [18].

The reagent when employed in this manner is particularly suited to the estimation of molybdenum in steels. Tungsten, if present, is precipitated with the molybdenum and various procedures have been put forward for the separation of these two elements [8, 15, 18].

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CACOTHELINE

(Nitrobruciquinone Hydrate)

$C_{21}H_{21}O_7N_3$

Mol. Wt. 427

Reagent for Tin

Cacotheline occurs as a yellow crystalline substance charring below 250°. With stannous tin in acid solution it gives rise to a violet coloured reduction compound, a similar result being given by the lower valencies of titanium, vanadium, niobium, molybdenum, tungsten, uranium, rhenium and europium.

Original work carried out in this laboratory, however, shows that when titanium salts are previously decolorised with hydroxylamine, no colour is given with cacotheline.

The reagent is used as a saturated solution in water, remaining stable for at least a fortnight.

Detection of Tin

The tin solution (reduced by zinc and hydrochloric acid if necessary), which should be not less than normal with respect to hydrochloric acid, is treated with solid hydroxylamine hydrochloride (to decolorise titanium salts) and a few drops of reagent solution added.

In presence of more than one part of tin per million parts of solution, a violet or pink colour is given which does not fade during fifteen minutes.

By this method, tin may be detected in presence of 5000 times as much antimony, bismuth, zinc, arsenic, magnesium, calcium, barium, strontium, cadmium, aluminium, or the alkali metals.

Tin may also be detected in presence of 1000 times as much lead, manganese, beryllium, and 500 times as much titanium.

With copper, nickel, cobalt, chromium and iron, colour interference occurs while molybdates and vanadates also invalidate the test, giving their own reduction colours. Small amounts of either a silver or a mercury salt cause interference.

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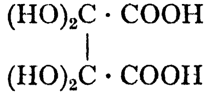
DIHYDROXYTARTARIC ACID



$$\begin{array}{c}(HO)_2C \cdot COOH \\ | \\ (HO)_2C \cdot COOH\end{array}$$

Mol. Wt. 182·1

Reagent for Sodium

The acid is a white cystalline powder, of melting-point about 115° with decomposition, and very soluble in water. It displays the characteristic instability associated with compounds containing two hydroxyl groups attached to the same carbon atom, and is liable to decompose both in the solid state and in aqueous solution.

The acid is characterised by the sparing solubility of its sodium salt. Many, but not all, of its salts with the heavy metals are insoluble [2]; it is therefore desirable that all metals except magnesium and the alkalis be removed before testing with dihydroxytartaric acid. The solubilities of the alkali dihydroxytartrates are given as follows [2]:

	Parts of salt dissolved by 100 parts of water at 0°
Cæsium	22·5
Rubidium	6·5
Ammonium	2·8
Potassium	2·7
Lithium	0·08
Sodium	0·04

Dihydroxytartaric acid has been used as a reagent for the detection and determination of sodium, and therefore an account of it is included in this book. In general, however, it will be found that uranyl zinc acetate (*q.v.*) or uranyl nickel acetate (*q.v*) is more satisfactory for this purpose.

General Conditions of Test

1. All metals except magnesium and the alkalis should be absent.

2. The solution to be tested should not be too dilute, and should be neutral.

3. The acid radicals present are, preferably, chlorides, sulphates, or nitrates. Carbonates and hydroxides are first neutralised. Phosphates and acetates give somewhat low results in the quantitative determination. Borates are anomalous—sodium borate does not give the characteristic reaction displayed by other sodium salts.

Detection of Sodium

The dihydroxytartaric acid is employed as a solution of its potassium salt. 1 g. of the acid is dissolved in 20 ml. of water, a drop of phenolphthalein solution added, and the solution cooled in an ice bath. Potassium hydroxide solution (N/1), previously cooled in ice, is added until a slight pink tint is observed. About 13 ml. are necessary. The pink tint fades, due to the action of atmospheric carbon dioxide—this is immaterial. The solution is preserved between 0° and 5°, and is preferably not kept for longer than a few hours.

The solution to be tested is cooled to 0° to 5°, an equal volume of the reagent added, the whole well mixed, and allowed to stand at 0° to 5°. The presence of sodium is indicated by the formation of a white crystalline precipitate seen under the microscope to consist of small diamond-shaped plates. The formation of the precipitate is facilitated by rubbing the tube with a glass rod. When very dilute sodium solutions are under test, several hours may elapse before any sign of a precipitate appears; however, after crystallisation has once commenced, development of the deposit occurs rapidly. In case of doubt, the solution may be seeded.

Whilst it will be appreciated that the figures given below are subject to considerable variation, it is felt that they will serve as a guide to the sensitivity of the reaction.

Concentration of solution (Na present as chloride)	Time elapsing between mixing and first appearance of a precipitate
1 of Na in 1,000	1 minute
1 of Na in 2,000	5 minutes
1 of Na in 5,000	2–3 hours
1 of Na in 10,000	4–6 hours

Determination of Sodium

The quantitative determination of sodium by means of dihydroxytartaric acid has been carefully examined by Radjy and Wood in a paper [6] from which the following details have been taken.

The concentration of sodium in the solution to be examined, should be adjusted to lie between 10 and 15 g. Na per litre in the form of chloride, sulphate or nitrate, and the solution should preferably be free from ammonium salts, although magnesium may be present in moderate amount.

The dihydroxytartaric acid reagent is prepared by dissolving 1 g. of the acid in 5 ml. of water, adding 35 ml. of ice-cold water and 5·5 ml. of a 1M solution of potassium carbonate. To 5 ml. of the sodium solution, contained in a small beaker, is added the whole of this quantity of reagent, with stirring, the temperature being maintained at 5° throughout. The mixture is allowed to stand at this temperature for about five hours, after which time the precipitate is filtered by suction on a 2 cm. diameter filter paper, washed with 10 ml. of ice-cold water, and both precipitate and paper are then together placed in an acidified permanganate solution.

This latter consists of a mixture of 100 ml. of N/10 potassium permanganate, 100 ml. of 5N sulphuric acid, 100 ml. of 6·3N phosphoric acid and 2 ml. of a vanadium catalyst. This last must be freshly prepared immediately before use and consists of a 0·05 per cent. aqueous solution of ammonium metavanadate acidified by the addition of a few drops of dilute sulphuric acid. After standing at room temperature for twenty minutes the solution is heated to 50° and the excess of permanganate is titrated with N/10 oxalic acid.

$$1 \text{ ml. N/10 } KMnO_4 = 0{\cdot}000767 \text{ g. Na.}$$

To the quantity of sodium thus found an addition of 0·0051 g. Na is made, to allow for the solubility (0·042 g. per 100 ml. at 5°) of sodium dihydroxytartrate in the precipitating liquor and wash water. From the results quoted in the paper referred to, an accuracy of about ±2 per cent. may be expected under the best conditions; if these are not adhered to, however, serious error may arise.

In the presence of ammonium salts low results are obtained, in the presence of magnesium salts slightly high results, whilst in the presence of both together the results are abnormally low.

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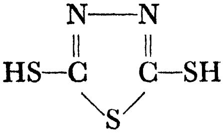
DIMERCAPTOTHIODIAZOLE



Mol. Wt. 150

Reagent for Bismuth

The reagent is a lemon-yellow powder, insoluble in water but soluble in alkalis and in alcohol. The alkaline solution is somewhat unstable, depositing sulphur on long standing, but even after standing for three months the solution is still suitable for use.

The reagent solution is prepared by dissolving 1 g. of dimercaptothiodiazole in 35 ml. N/10 potassium hydroxide and filtering. The solution gives coloured precipitates in neutral or slightly acid solutions with metals of groups I and II of the qualitative analytical table.

Mercurous Silver	pale yellow
Lead Tin Antimony	lemon yellow
Copper	yellow-brown
Mercuric	black
Bismuth	brick-red

A number of other metals and acid radicals, not mentioned in the literature, also yield precipitates in acid solution. Palladium and platinum give blood-red and orange-yellow precipitates respectively, while thallium and gold salts give yellow precipitates. Various acid radicals, viz., tungstates, arsenates, arsenites, selenates, selenites, molybdates, chromates and vanadates, form insoluble coloured complexes in acid solution.

Detection of Bismuth [1, 2, 3, 5]

With the exception of palladium, bismuth is the only metal which gives rise to a red insoluble complex. The reagent is therefore advocated as a confirmatory test for bismuth in qualitative analysis after separation from other metals of the sulphide group. A red precipitate is obtained in concentrations as low as one part in 25,000 parts of solution.

A procedure has been evolved employing dimercaptothiodiazole for the detection of lead in petrols, where it is claimed 0·02 mg. of lead may be detected in a 4 ml. sample [7].

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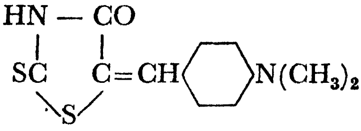
p-DIMETHYLAMINOBENZALRHODANINE



Mol. Wt. 264

Reagent for Silver, Copper (ous) and Mercury

A brilliant red crystalline powder, of indefinite melting-point’ decomposing gradually as the temperature rises above 200° [1]. The compound is insoluble in water, slightly soluble in alcohol, and somewhat more so in acetone. It is used as a 0·03 per cent. solution in acetone, and is especially recommended for the detection of silver, for which metal it may, under suitable conditions, be made specific. The reagent should always be employed in acid solution, never in alkaline, since in the latter case, tautomeric changes in the rhodanine portion of the molecule take place, which cause the reagent to react with almost all the heavy metals.

In acid solution, a positive reaction is given by the following:—silver, mercury (ous and ic), copper (ous), gold, platinum and palladium.

Detection of Silver [2, 5]

To 20 ml. of the solution to be tested, which should be approximately neutral, 2 ml. of N/1 nitric acid are added, followed by 0·5 ml. of a 0·03 per cent. solution of the reagent in acetone. In the presence of silver a reddish coloration is produced. It is possible to detect one part of silver in 5,000,000 parts of water by this means, whereas the use of chloride ion as a reagent will, under the same conditions, only give a visible reaction with one part of silver in 400,000 parts of water.

Under these conditions, all the metals mentioned above give very similar colours to that furnished by silver. To make the reaction specific for silver, in the presence of one or more of these metals, two modifications are available:

(*a*) The addition of hydrochloric acid. This must be used when mercuric ions are also present.

(*b*) The addition of potassium cyanide. This must *not* be employed when copper (either cuprous or cupric), nor yet when mercurous ions are also present, but must be used when mercuric, gold, platinum, or palladium ions are likely to interfere.

The technique in these two cases is given below:

(*a*) With hydrochloric acid (*i.e.* in the presence of mercuric ions). To 20 ml. of the solution to be tested (as nearly as possible neutral), 2 ml. of N/1 nitric acid are added, followed by 0·5 ml. of a 0·03 per cent. solution of the solid reagent in acetone, and 0·5 ml. of N/10 hydrochloric acid. This quantity of acid has no effect on the colour produced by concentrations of silver approaching the limit of sensitivity of the test, but discharges the colour due to even large amounts of mercuric ions. If more than this amount of hydrochloric acid be added, the coloration produced by silver itself is discharged. It is further important that the hydrochloric acid be added after the rhodanine reagent, and not before, since if the acid be added first the colour due to silver is not produced.

(*b*) With potassium cyanide (*i.e.* in the presence of gold, platinum, or palladium ions). To 20 ml. of the solution to be tested, as nearly as possible neutral, 0·5 ml. of a 10 per cent. solution of potassium cyanide is added, followed by 0·5 ml. of a 0·03 per cent. solution of the reagent in acetone, and 2 ml. of N/1 nitric acid—this last being added slowly. A little more acid may be used if necessary, a slight excess being not detrimental. The quantity of cyanide is, however, somewhat critical; with too little, the colour produced by gold is not suppressed, with too much, the sensitivity of the reaction for silver is greatly reduced.

Colorimetric Determination of Silver [13, 14]

A technique has been proposed [13] which is claimed to reduce the liability of interference by mercury, in which a solution of the reagent in amyl alcohol is used, and the red complex later dispersed to form a colloidal suspension by the addition of ethyl alcohol and glycerol. The suspension may then be compared colorimetrically with standards.

Detection of Copper [4, 5]

Cuprous ions give a vivid violet-coloured precipitate or coloration in neutral solution, in solutions acidified with dilute nitric acid, in solutions containing both nitric and hydrochloric acids (technique (*a*) above), and also in solutions containing potassium cyanide and nitric acid (technique (*b*) above). The sensitivity is stated to be one part of copper (ous) in 3,000,000 parts of water. Cuprous ions are likely therefore seriously to interfere with the detection of silver, since they give colours under all possible modifications of the test. To avoid this difficulty, the solution under test should be subjected to oxidising conditions, since when copper is present in the cupric form it will not interfere with the test for silver in acid solution.

Cupric ions give a reddish colour with the reagent in neutral solution, but no colour when the solution is acid, either with nitric or hydrochloric acids, or both. If cyanide is present, this converts the cupric into the cuprous form, which then yields the violet precipitate characteristic of this latter state..

Detection of Mercury [5]

Mercurous ions yield with the reagent in neutral solution, or in solution acidified with dilute nitric acid, a brilliant purple coloration. In the presence of hydrochloric acid mercurous chloride is, of course, precipitated, whilst in the presence of cyanide, metallic mercury is thrown down.

Mercuric ions furnish a reddish colour in neutral solution, or in the presence of dilute nitric acid; this colour is discharged by either hydrochloric acid (technique (*a*) above), or in the presence of cyanide (technique (*b*)). The depth of colour developed by mercuric salts depends upon their degree of ionisation.

The sensitivity for both forms of mercury (when strongly ionised) is stated to be about one part in 2,000,000 parts of water.

Colorimetric Determination of Mercury [15]

The reagent has been employed for the quantitative determination of small quantities of mercury and applied to the determination of mercury in organic materials.

Spot Tests [3, 6, 7, 8, 9, 10, 11]

The conditions set out above for the detection of the various metals may be readily applied to the spot technique, either on a tile or on absorbent paper.

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DIMETHYLGLYOXIME

(Diacetyldioxime)

$CH_3 \cdot C(:NOH) \cdot C(:NOH) \cdot CH_3$

Mol. Wt. 116·1

Reagent for Nickel, Palladium, Bismuth and Iron

Dimethylglyoxime is a white crystalline powder which melts at 235°–237° with decomposition. It dissolves in alcohol forming a clear colourless solution.

Dimethylglyoxime is used for the detection and gravimetric determination of nickel and palladium, and for the detection of bismuth. An acid solution of a nickel salt containing dimethylglyoxime deposits a red crystalline precipitate when made slightly alkaline. The red compound has the composition $C_8H_{14}N_4O_4Ni$. Certain other metals give coloured precipitates with dimethylglyoxime but cobalt, zinc and manganese do not. The palladium compound, which is precipitated from dilute mineral acid solution, is yellow and can be weighed as $C_8H_{14}N_4O_4Pd$, or can be ignited and weighed as metallic palladium. Bismuth salts produce with dimethylglyoxime in the presence of a chloride and excess ammonia a yellow precipitate.

Detection of Nickel

A 1 per cent. solution of the reagent in alcohol is prepared. The slightly acid test solution is heated to boiling, a few drops of the reagent solution are added and ammonia solution is run in until the mixture is alkaline. The whole is boiled and cooled. Red needles are formed in the solution in the presence of nickel but, if the amount be exceedingly small, they may not appear until the solution is cold. One part in 2,000,000 can be detected by this method. Cobalt does not interfere with the reaction unless present in great excess.

Nickel may be detected in cobalt salts by adding dimethylglyoxime solution to the boiling dilute solution and then sodium acetate (1 g. to every 10 ml. of solution). The mixture is cooled and filtered and the filter paper examined for red crystalline precipitate. A more sensitive method is to dissolve 2 grams of the salt in 20 ml. of water, add 40 ml. of 10 per cent. potassium cyanide solution, 10 ml. of N/1 sodium hydroxide and 10 ml. of hydrogen peroxide (20 volumes). The mixture is then heated in a water-bath for ten minutes, 20 ml. of 10 per cent. ammonium chloride solution and 2 ml. of dimethylglyoxime solution are then added, and the solution evaporated on a water-bath. Red flocks of the nickel complex separate during the evaporation or, if only traces of nickel are present, the yellow crystalline residue will be tinged with pink.

Detection of Nickel by the Spot Reaction [70]

One drop of the solution to be tested is placed on a filter paper and on to it are dropped in turn, one drop of 1 per cent. alcoholic dimethylglyoxime solution and one drop of dilute ammonia. The presence of nickel is indicated by a red spot or ring. Alternatively the test solution may be dropped on to a paper previously soaked in dimethylglyoxime solution and dried. One part in 300,000 can be detected by this means.

Detection of Bismuth [64]

The acid solution containing bismuth and a chloride is treated with a little 1 per cent. dimethylglyoxime solution and the whole is then made strongly alkaline with ammonia. An intense yellow precipitate is formed in the presence of much bismuth, and a yellow colour is produced when traces of the metal are present. One part of bismuth in 50,000 parts of water may be detected by this reaction. If excess of tartrate be present, the reaction is completely inhibited. Thus nickel may be detected in the presence of bismuth by adding a tartrate before the dimethylglyoxime. Arsenic, antimony, tin, cobalt, iron, manganese and cadmium do not hinder the detection of bismuth.

Determination of Nickel

(*a*) *Gravimetric.*—The solution, containing not more than 0·1 g. nickel per 200 ml. solution, is rendered slightly acid and boiled. An excess of dimethylglyoxime solution is then added (0·4 g. dimethylglyoxime for each 0·1 g. nickel) and then ammonia is run in until the solution is slightly alkaline. The precipitate is allowed to stand for one hour and filtered into a tared Gooch crucible. After washing with hot water the precipitate is dried at 115° for forty-five minutes and weighed.

$$\text{Wt. of precipitate} \times 0{\cdot}2032 = \text{Wt. of Ni.}$$

The method may be applied to the determination of nickel in the presence of cobalt, manganese and zinc and, with modification, to the separation of nickel from iron and chromium [7].

The determination of nickel in steel can be carried out without the removal of the iron, if sufficient tartrate be present to prevent the precipitation of the iron by ammonia [7].

(*b*) *Volumetric* [89].—The nickel-glyoxime complex washed free from dimethylglyoxime, is dissolved in 15 ml. sulphuric acid, about 12N, and the filter washed well with water. The filtrate and washings are concentrated to a volume of 25 ml., 50 ml. ferric sulphate solution containing about 40 g. per litre is added and the heating continued for five minutes. The solution is cooled, diluted with

150 ml. water containing 3 ml. phosphoric acid (1·7) and titrated with potassium permanganate.

1 ml. N/10 potassium permanganate = 0·0007335 g. nickel.

An alternative method of titration [94], which has been suggested, is to dissolve the nickel complex in mineral acid and to determine the nickel in solution by the cyanometric titration.

(*c*) *Colorimetric* [61].—In the absence of cobalt and copper, the solution is treated with bromine water in slight excess. Then the bromine colour is removed by means of ammonia and finally a few drops of dimethylglyoxime solution are added.

No crystals of the nickel compound are deposited, but a red colour appears, the intensity of which is measured in a colorimeter by comparison with a tint prepared from a known amount of nickel.

Detection of Iron [31, 43]

Dimethylglyoxime has been proposed as a reagent for the detection of ferrous iron; an ammoniacal solution of the ferrous dimethylglyoxime complex shows an intensely red solution and in this way it is possible to detect one part of ferrous iron in 50,000,000 parts of solution. For further details reference to the literature should be made.

Determination of Palladium [22, 23, 24, 43, 56, 58, 63, 88, 91, 100, 102, 108, 109]

To a solution of palladium containing 0·1 g. of palladium or less in 300 ml. of solution acidified with 1 to 5 ml. of concentrated hydrochloric or sulphuric acid, is added an excess of an alcoholic solution of the reagent (0·4 g. dimethylglyoxime for each 0·1 g. palladium). Nitrate must not be present in the solution; the presence of nitrate results in small quantities of palladium being retained in solution. The precipitate is allowed to stand for one hour, preferably in a warm place, filtered and washed with distilled water. The precipitate may be dried to constant weight at a temperature not exceeding 110°, one hour is usually sufficient, and weighed as $PdC_8H_{14}N_4O_4$.

$$\text{Weight of ppt} \times 0{\cdot}3167 = \text{Wt. of Pd.}$$

Alternatively the precipitate may be ignited and weighed as metallic palladium.

Gold and platinum are the only metals which interfere with this estimation. Gold must be removed before precipitating palladium with dimethylglyoxime. Platinum tends to co-precipitate with the palladium; when this metal is present a double precipitation is necessary and if the first precipitation is made in the cold the quantity of platinum so precipitated is minimised.

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DIPHENYLCARBAZIDE

$C_6H_5 \cdot NH \cdot NH \cdot CO \cdot NH \cdot NH \cdot C_6H_5$

Mol. Wt. 242·3

Reagent for Mercury, Cadmium, Lead, Chromium and Magnesium

Diphenylcarbazide is a white crystalline powder which slowly assumes a pink colour on exposure to air. In solution this colour change is more rapid. The substance melts at 167° to 169°.

Diphenylcarbazide has been used for the detection, and in some cases for the colorimetric estimation of the following elements—cadmium, chromium (as chromate), mercury and molybdenum. Cobalt, copper, lead, nickel and silver also react to give colours, but the sensitivity of the reactions is not great and unless elaborate precautions are taken, each of these metals will interfere with the detection of the others. Further, it has been suggested [7, 14, 20, 22] that the detection of mercury by means of diphenylcarbazide is dependent upon the formation of diphenylcarbazone in the reagent solution by oxidation, either with air or with ions of high valency ($Fe^{\cdots}$ $Cu^{\cdots}$ etc.). Diphenylcarbazone is much more suitable for the detection of mercury than is diphenylcarbazide and therefore the detection of mercury is described fully in the monograph on the former reagent.

The methods which are of importance are:—

(*a*) Detection of cadmium.
(*b*) Detection of magnesium.
(*c*) Detection of mercury by the spot-reaction.
(*d*) Detection of chromium as chromate.
(*e*) Use of diphenylcarbazide as an internal indicator in iron and vanadium titrations.
(*f*) Use of diphenylcarbazide or diphenylcarbazone as indicator in the titration of chloride, iodide and cyanide with mercuric nitrate or silver nitrate solution.

(a) Detection of Cadmium [14]

Two methods are available.

1. To the solution to be tested sodium acetate is added to reduce the acidity if necessary and a few drops of a saturated alcoholic solution of the reagent added. A violet colour is produced in the presence of cadmium. One part in 37,000 may be detected in this way in the absence of interfering metals.

2. The neutral or slightly acid solution is spotted on to a filter paper previously soaked in alcoholic reagent solution and dried. The paper is held over strong ammonia solution. A violet-blue spot, surrounded by a reddish colour, indicates the presence of cadmium. A modification of the method is used to prevent interference from copper [14].

(b) Detection of Magnesium [20, 23, 24]

Magnesium compounds when treated with an alkaline solution of diphenylcarbazide give a violet-red colour. The method has been applied to the detection of magnesium in minerals.

(c) Detection of Mercury by the Spot-reaction

One drop of the neutral test solution is dropped on to a filter paper previously soaked in fresh 1 per cent. alcoholic diphenylcarbazide solution. Mercury produces a violet or blue spot which is specific if the solution is N/5 with regard to nitric acid, and if chromates and molybdates are absent.

(d) Detection of Chromium as Chromate [3, 22, 28, 33, 62

In acid solution chromates oxidise diphenylcarbazide forming a deep violet-red colour.

The reagent is prepared by dissolving 0·2 g. of the substance in 10 ml. of acetic acid and diluting to 100 ml. with water. The chromate in solution is made acid with hydrochloric or sulphuric acid and the above reagent added (2 or 3 drops per 10 ml. of solution). A violet-red colour develops in a few seconds in the presence of chromate. The reaction is more sensitive than the well-known ether-peroxide method and can be conducted in the presence of aluminium and nitrates. Thus traces of chromium may be detected in the iron group precipitate. Excess of hydrogen peroxide masks the reaction somewhat. One part of chromium can be detected in 5,000,000 parts of solution by this method.

An extension of this method has been made by Jones [29] who has determined small traces of lead by precipitation as lead chromate followed by colorimetric estimation of the chromate present. *See also* [31, 69, 74].

(e) Use of diphenylcarbazide as an internal indicator in the dichromate titration of iron [5, 8, 42, 54]

The solution of iron in the ferrous state and containing hydrochloric acid is diluted to about 500 ml., 30 ml. of saturated mercuric chloride solution, 20 ml. of manganese sulphate mixture,* 10 ml. of hydrochloric acid (1·16) and 1 ml. of indicator solution † are added. The solution thus formed is titrated with N/10 potassium dichromate until the red colour first formed fades to a clear green. It is well to carry out a blank titration using a little ferric chloride solution and the reagents described.

A similar method is described for the estimation of vanadium in steel [12].

(f) Use of diphenylcarbazide or diphenylcarbazone as indicator in the titration of chloride with mercuric nitrate solution [35, 38, 39, 43, 51]

The neutral chloride solution (NaCl) is titrated with N/10 mercuric nitrate solution (16·23 g. solid salt and 10 ml. 5N nitric acid per litre of solution) using a few drops of 2 per cent. alcoholic solution of the indicator.

The end point is marked by the appearance of an intense violet colour.

The process appears to be very much dependent upon the conditions of acidity, etc., and cannot yet be recommended for use with solutions containing unknown constituents.

Similar processes have been described for cyanides [37, 65], iodides [43, 55, 75] and bromides [54, 76].

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* 200 g. manganese sulphate, 250 g. sulphuric acid (1·84), and 170 g. phosphoric acid (1·75) diluted to 2 litres.

† 0·1 g. diphenylcarbazide dissolved in 30 ml. acetic acid and diluted to 100 ml.

DIPHENYLCARBAZONE

$C_6H_5 \cdot NH \cdot NH \cdot CO \cdot N : N \cdot C_6H_5$

Mol. Wt. 240·3

Reagent for Mercury

Diphenylcarbazone is an orange crystalline powder which dissolves in alcohol to form a red solution. It has no definite melting-point but decomposes at about 150°. For the detection of mercury a saturated solution in alcohol is used.

Detection of Mercury [3, 6, 7, 19, 20, 21, 26, 27, 38, 48, 61]

The solution to be tested is made neutral or faintly alkaline (optimum pH 7 to 8) by adding sodium acetate. Usually about 1 g. for every 10 ml. of solution is sufficient, and one drop of the reagent solution is added for each 10 ml. of solution. A violet or blue colour develops in the presence of mercury. One part of mercury can be detected in 10,000,000 parts of water by this reaction.

The following acid radicals should not be present in large quantity since they greatly impair the sensitivity of the reaction—chlorides, bromides, iodides and cyanides. Acetates, nitrates, sulphates, oxalates and phosphates do not interfere.

Lead, copper, tin, cadmium, nickel and cobalt all give deep colours with diphenylcarbazone and thus they seriously interfere with the detection of small traces of mercury. Silver, antimony, arsenic, iron, chromium, aluminium, manganese and zinc interfere to a slight extent if present in fairly small amounts, and calcium, strontium, barium, potassium, and sodium have no effect.

Special methods have to be adopted for the detection of mercury in the presence of organic substances. The substance is boiled with hydrochloric acid and potassium chlorate to convert the mercury into mercuric chloride and then pieces of zinc are allowed to stand in the solution for about twenty-four hours. The zinc is treated with chlorine water and the liquid so obtained tested as described above.

A method has also been devised for the detection of mercury in the presence of the metals of the hydrogen sulphide group [26].

Detection of Mercury by the Spot-reaction [36]

A drop of the neutral test solution is allowed to fall on a filter paper previously soaked in diphenylcarbazone solution. Both mercurous and mercuric ions react to produce a violet spot, but of these only the mercuric compound is said to be soluble in benzene. We find that the spot produced by mercuric chloride is soluble but that the spot produced by mercuric nitrate is not. A further investigation of this technique is necessary.

Quantitative determination of chlorides and cyanides using mercuric nitrate solution and diphenylcarbazone as indicator [35, 37, 38, 39, 42, 43, 64, 65]

(*See under* diphenylcarbazide.)

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DIPHENYLTHIOCARBAZONE

' Dithizone '

$C_6H_5 \cdot NH \cdot NH \cdot CS \cdot N : N \cdot C_6H_5$

Mol. Wt. 256·3

Reagent for Lead and other metals

Diphenylthiocarbazone is a nearly black powder which is insoluble in water but dissolves in certain organic liquids yielding solutions of intense green colour. The solution in carbon tetrachloride has been used for analytical purposes, but a solution in chloroform is generally to be preferred since the reagent is more readily soluble in this solvent. Such solutions are unstable due to air oxidation, but that in carbon tetrachloride may be preserved for a considerable period if protected by a layer of aqueous sulphur dioxide solution.

The reagent combines with basic substances. Thus, if the solution in chloroform is shaken with dilute aqueous ammonia the dithizone is extracted more or less completely from the organic layer and forms a yellow to deep orange solution in the aqueous layer. When, however, a solution of a cadmium salt containing 5 per cent. of sodium hydroxide is shaken with a chloroform solution of the reagent, the cadmium enters the organic layer as dithizonate [58].

With certain metals dithizone forms compounds of intense and characteristic colours. These compounds are generally much more soluble in organic solvents than water. Consequently a solution of a salt of the metal shaken with a chloroform or carbon tetrachloride solution of the reagent will impart its characteristic colour to the organic layer. The reagent has been applied in this manner to the detection of a number of metals, but its main use has been for the extraction and estimation of lead. Methods have also been evolved for the extraction and estimation of zinc, mercury, copper, silver, cobalt, cadmium and thallium, as may be seen from the titles of papers given in the bibliography.

The noble metals also react.

Detection of Lead

Lead in ammoniacal solution imparts a brick-red colour to the reagent solution. A rather similar colour is obtained in the absence of lead due to some of the ammonium salt of the reagent remaining in the chloroform. Addition of potassium cyanide causes complete extraction of excess reagent into the aqueous layer, and at the same time forms complexes with certain metals which would otherwise interfere.

Conditions may be varied to some extent, with consequent variation of the sensitivity of the reaction, but under the following conditions one part of lead in 20,000,000 parts of solution may be detected.

To 10 ml. of the solution are added 1 ml. of 10 per cent. potassium cyanide solution and a few drops of ammonia. The solution is then shaken vigorously in a test tube with 2 ml. of diphenylthiocarbazone in chloroform (3–5 mg. per 100 ml.). Bismuth gives an orange colour but it is possible to detect lead in presence of considerable excess of bismuth. Stannous tin must be oxidised to the stannic condition. Thallium gives a similar colour to lead.

When necessary, sodium potassium tartrate may be added to prevent precipitation of hydroxides or basic salts. The addition of tartrate and of many other salts tends to cause the excess reagent to remain in the chloroform. This residual colour may be green or red or an intermediate colour according to the pH of the aqueous layer which, in these circumstances, is buffered. The colour change of the reagent itself from green to red is completed only at about pH 11. It is apparent that under all but the simplest conditions results must be interpreted with caution and should, where possible, be compared with blanks.

Determination of Lead

Dithizone finds its most important application as a reagent in the quantitative separation of lead from other metals. The lead is extracted under appropriate conditions from aqueous solution with a freshly made chloroform solution of the reagent. The lead may be determined either by a colorimetric examination of the extract, or by evaporation of the extract, wet oxidation of the residue and subsequent estimation as sulphide colorimetrically, or the lead may be precipitated as chromate from a solution of the oxidised residue and the chromate ion titrated. The method outlined below is suitable for the determination of lead in organic materials containing iron and other non-interfering metals.

A suitable quantity of the material is oxidised with nitric and sulphuric acids or with hydrogen peroxide and sulphuric acid and the excess oxidising agent evaporated. The residue is diluted with water, potassium cyanide and citric acid added, the latter to retain iron in solution, and made alkaline with ammonia. The solution is extracted three times with 10 ml. of diphenylthiocarbazone solution (0·1 per cent. in chloroform), each extract being washed with an equal quantity of water. The combined extracts are evaporated to dryness, heated with a small quantity of sulphuric acid and evaporated to fuming several times with small quantities of hydrogen peroxide (30 per cent.) until colourless. The residue is then dissolved in water, a suitable aliquot portion is transferred to a Nessler glass, treated with 2 g. ammonium acetate, 5 ml. ammonia solution 5N, 1 ml. of 10 per cent. potassium cyanide, and 2 drops of 20 per cent. sodium sulphide solution. The colour developed is compared with standards prepared in a similar manner from a standard solution of lead nitrate. A suitable standard solution of lead is prepared by dissolving 1·6 g. of lead nitrate in nitric acid and diluting with water to 1 litre. For use this solution is diluted 100 times. Of the diluted solution 1 ml. = 0·01 mg. Pb.

It has been stated [82] that unduly large amounts of iron may conveniently be removed in acid solution with cupferron, the iron complex being extracted with chloroform. The aqueous layer is then evaporated to white fumes with concentrated sulphuric acid and nitric acid to destroy excess cupferron, and the lead in the residue determined by dithizone in the usual way. An advantage of this method is that ferric iron is liable to oxidise the reagent when cyanide is present in excessive amount.

Determination of other metals

Copper may be determined by separation using a method similar to that described above, followed by colorimetric examination of the extract, or by destruction of the organic material followed by colorimetric assay with rubeanic acid.

The separation of zinc from lead has been described by Sylvester and Hughes [51]. They dissolve the inorganic ash (from a food sample) in 5 ml. hot 5N hydrochloric acid, add 30 ml. water and 10 ml. 5N ammonium acetate solution. From this solution (pH about 4·5) zinc is removed by shaking with dithizone in chloroform, leaving the lead in the aqueous layer.

An alternative separation is as follows: shake the chloroform layer of mixed zinc and lead dithizonates with 5 per cent. potassium thiocyanate solution (aqueous) when zinc is removed and all the lead remains behind in the organic layer.

In some circumstances a titrimetric procedure is possible, in which the test solution, contained in a separating funnel, is titrated with a chloroform solution of the reagent, the lower layer being frequently withdrawn, until the chloroform layer remains green in colour. In this manner, for example, silver may be determined in presence of lead, zinc, cadmium, arsenic, antimony, bismuth, copper, mercury and gold [34].

It is stated [84] that bismuth may be removed from its admixture with lead by shaking the solution of mixed nitrates in nitric acid (pH of the solution about 2·0) with dithizone in chloroform. Our experience indicates that a somewhat less acid solution is required for complete removal of bismuth. This view is confirmed by Wichmann [79] who quotes a provisional table giving the extraction pH for several metals.

Metal	pH for 100 per cent extraction
Zinc - - - -	6·5–10·0
Tin (ous) - - -	3·5– 8·3
Bismuth - - -	4·2– 8·7
Lead - - - -	8·7–10·9
Cadmium - - -	12·2 upwards
Thallium - - -	10·7 „
Copper - - -	5·2 „
Silver - - - -	1·5 „
Mercury - - -	2·0 „

According to Fischer and Leopoldi [26], dithizone is specific for zinc in approximately neutral solution containing sodium thiosulphate and potassium cyanide.

In addition to zinc, copper, mercury, silver, bismuth and cadmium are removed by a solution of dithizone at pH 4·5. From this extract zinc, bismuth, and cadmium are removed with dilute hydrochloric acid (silver is removed as insoluble chloride).

The extraction of a solution containing 5 per cent. of sodium hydroxide with amounts of lead, zinc and cadmium, by shaking with dithizone in chloroform, removes cadmium only, leaving the other metals in the aqueous layer.

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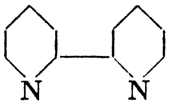
αα′-DIPYRIDYL



Mol. Wt. 156·2

Reagent for (ferrous) Iron and Molybdenum

αα′-Dipyridyl is a white crystalline substance melting at 68–70° and soluble in dilute acids. On addition of the reagent to solutions containing ferrous iron a red colour is obtained, but with ferric iron it gives no colour. Ferrous iron may therefore be detected and determined colorimetrically in presence of much greater concentrations of ferric iron, and αα′-dipyridyl has been successfully applied to this purpose, particularly in certain biological work. The intensity of colour is said to be independent of pH change within wide limits and to conform closely to Beer's law. In these and other respects αα′-dipyridyl is said [25] to be superior to certain reagents for ferric iron and may therefore be advantageously substituted for them by reducing the iron to the ferrous condition.

The reagent solution is prepared by dissolving 1 g. of αα′-dipyridyl in 10 ml. N hydrochloric acid and diluting to 100 ml. with water.

Detection of Ferrous Iron

To the solution under test are added a few drops of the reagent solution, the pH being maintained between 3·5 and 8·5. A red colour is developed immediately if ferrous iron be present, minimal amounts giving a rose pink. In the absence of other coloured substances 0·1 γ ferrous iron may be detected in 1 ml. of solution.

Detection of Ferrous and Ferric Iron

The procedure is similar to that described for ferrous iron except that a reducing agent is added. The acid solution is treated with sodium sulphite, buffered with ammonium acetate and a few drops of the reagent added. Presence of phosphate, citrate or oxalate retards reduction by sulphite and quinol should then be used instead [19]. The solution must be acid in either case. Several other reducing agents have been employed,—sodium hydrosulphite, sulphur dioxide solution, titanous chloride, *p*-hydroxyphenylglycine and hydroxylamine, but none of them seems to offer any special advantage.

Colorimetric Estimation of Iron

The procedure for colorimetric estimation is simply an adaptation of the methods already described. Conditions should, of course, be standardised, and a fair excess of reagent added, since at very low excess the colour developed is somewhat dependent on the amount in excess. For visual comparison standards may be prepared from known amounts of iron and dipyridyl and are said to be stable for at least 3 years [2]. Standardised conditions for photometric work have been described by Schulek and Floderer [24], Moss and Mellon [30], and Delory [31].

Interference

A number of other metals form compounds with *αα′*-dipyridyl, but in many cases they are colourless and sufficiently soluble, and only necessitate the use of sufficient dipyridyl. The zinc compound is sparingly soluble, and the copper compound is pale blue, but Schulek and Floderer [24] determined ferrous iron in presence of ten times its quantity of the following:—zinc, copper (+potassium cyanide), aluminium, manganese, mercury, ferric iron (+phosphoric acid). Larger quantities of copper may conveniently be removed as cuprous thiocyanate when total iron is to be determined. Ferric ions may also be decolorised by the addition of fluoride. The white precipitate given by mercury may be prevented by addition of sodium chloride [3]. Moss and Mellon [30] have carried out extensive experiments with a wide range of metals and acid radicals, and specify the maximum amount permissible in photometric work. Oxalate was found to have the most pronounced disturbing effect and must be eliminated.

αα′-Dipyridyl as Indicator in the Titration of Ferrous Iron [9]

To the ferrous solution, containing 0·1 to 10 mg. Fe, in 50 ml. and sufficient hydrochloric acid to produce N/1 concentration, are added 5 drops of the reagent solution prepared by dissolving 0·25 g. *αα′*-dipyridyl in 50 ml. of water and 50 ml. ammonia solution (s.g. 0·880). The solution is titrated with 0·01 N ceric sulphate solution to the disappearance of the pink colour. The end point is quite sharp.

Ferric iron may be reduced and titrated similarly. The use of a silver reductor [7] enables iron to be determined in presence of vanadium, chromium and titanium.

Detection of Molybdenum [17]

A drop of the solution is treated in a white porcelain vessel with 2 drops of *αα′*-dipyridyl solution (3 per cent. in alcohol), and 1 drop of stannous chloride solution (10 g. in 20 ml. strong hydrochloric acid). The presence of molybdenum gives rise to a red-violet colour or precipitate according to the amount present. One may thus detect 0·4 γ Mo in a concentration of 1 : 100,000. No reaction is given by rhenium, vanadium, arsenic or uranium. Should tungsten be present it is necessary to prevent interference by the addition of tartaric acid. For details of this procedure the reader is referred to the literature.

αα′-Dipyridyl has also been used for the purpose of preventing the interference by iron with the determination of copper by sodium diethyldithiocarbamate [23, 29], and for a similar purpose in other analytical processes [15].

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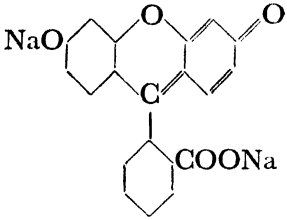
FLUORESCEIN, SODIUM SALT

(Soluble fluorescein, Uranine)



Mol. Wt. 376

Reagent for Bromide

The disodium salt of fluorescein is an orange-red powder, soluble in water and in alcohol. The aqueous solution shows a strong fluorescence, even in extreme dilution. Fluorescein readily reacts with free bromine to form eosin and this has been made the basis of a method for the detection and determination of bromides.

Detection of Bromide [13]

The following solutions are required:—

(*a*) Fluorescein solution, 0·02 per cent. in water.

(*b*) A solution of chloramine T containing approximately 15 g. per litre.

(*c*) A buffer solution prepared by dissolving 136 g. sodium acetate cryst. in a litre of water and adding 100 ml. N acetic acid. The pH of this solution should be 5·5 to 5·6.

(*d*) A solution of 50 g. sodium hydroxide and 5 g. sodium thiosulphate in a litre of water.

Make the solution under test nearly neutral and to 25 ml. add 0·2 ml. fluorescein solution, 1 ml. of buffer and 0·2 ml. chloramine T. Allow to stand for two minutes and then add 0·2 ml. of the alkaline-thiosulphate solution. The appearance of a red or pink coloration indicates the presence of bromide. By comparison with a blank test it is possible to detect one part of bromine in 10,000,000 parts of solution. Iodides interfere, but can be eliminated by boiling with sodium nitrite and a little dilute acid. Substances which reduce chloramine T naturally interfere with the test, as do metals which give rise to coloured ions.

When the test solution is coloured a modified technique is advocated [7]. Add to the test solution 5 ml. of a saturated solution of potassium permanganate and 5 ml. of dilute sulphuric acid and warm gently. Hold over the test tube a paper which has been immersed previously in the fluorescein solution and allowed to dry. The appearance of a pink stain indicates the presence of a bromide. This procedure is less sensitive than the former, but even so, 0·1 mg. bromine can readily be detected.

Determination of Bromide [13]

The test solution should be adjusted to contain from 0·0025 to 0·05 mg. bromine. The first procedure detailed above is carried out and the colour obtained is compared with a series of standards containing known amounts of potassium bromide.

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FORMALDOXIME

$H \cdot CH = N \cdot OH$

Mol. Wt. 45·0

Reagent for Manganese

This substance, a liquid of boiling-point 85°, is used as a 5 per cent. *w*/*v* aqueous solution.

Detection and Determination of Manganese

To the solution under test (50 ml.) are added three drops of reagent solution, followed by excess 5N ammonia or sodium hydroxide. Manganese, if present in a concentration of one part or more per 25,000,000 parts of solution, will be shown by a red-brown colour.

In this manner manganese may be detected in presence of at least 1000 times as much lead, mercury, silver, bismuth, copper, cadmium, arsenic, antimony, tin, aluminium, zinc, barium, strontium, calcium, magnesium, beryllium, thallium, tungstate, molybdate or vanadate.

Copper gives a colour with the reagent which is discharged by cyanide, the manganese colour being unaffected. In presence of beryllium, the solution must be made alkaline with ammonium carbonate, while large excesses of tin and vanadate require the use of blank tests.

For manganese concentrations between 0·2 and 5·0 p.p.m., a direct colorimetric estimation is possible, since colour and concentration are in proportion.

Large amounts of iron, chromium, chromate, nickel and cobalt produce colours which mask the test. Waldbauer and Ward, however, co-precipitate the manganese and cobalt as ammonium phosphates, filter off, redissolve in 5N hydrochloric acid and reprecipitate. After this treatment, the cobalt content of the precipitate no longer is sufficient to hinder the direct colorimetric estimation. The precipitate is dissolved in 5N hydrochloric acid and tested as above.

Interference due to ferric iron may be very effectively removed, however, by precipitation with a strong aqueous suspension of zinc hydroxide (prepared by the addition of ammonia to zinc sulphate solution). The ferric hydroxide is filtered off and three drops of reagent solution followed by five drops of 5N sodium hydroxide added to the filtrate. In this way manganese may be detected even if originally accompanied by 10,000 times as much iron.

Sideris uses cyanide to minimise the iron colour, while Wagenaar [9] removes the iron as basic acetate.

In his later paper Sideris describes the removal of interference due to excess phosphate by precipitation with lead acetate solution, with subsequent removal of excess lead with sodium sulphate solution.

The reagent, first used by Bach in 1899 to detect copper, has also been employed by Denigès to detect nickel in excess cobalt.

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α-FURIL DIOXIME

$C_4H_3O \cdot C(:NOH) \cdot C(:NOH) \cdot C_4H_3O$

Mol. Wt. 220·2

Reagent for Nickel

In consequence of its greater sensitivity for nickel α-furil dioxime has some advantage over dimethylglyoxime for the detection and determination of this metal, particularly when the latter is present in minute amount. The furil compound will detect one part of nickel in 6,000,000 parts of solution as against a sensitivity of one in 2,000,000 in the case of dimethylglyoxime.

The reagent is only slightly soluble in cold water. A 2 per cent. alcoholic solution is therefore employed in analytical practice.

Detection and Determination of Nickel

The nickel solution is rendered slightly alkaline by the addition of ammonia and a 2 per cent. alcoholic solution of furil dioxime added in excess. A red precipitate is produced immediately, but when the concentration approaches the limit of sensitivity (1 : 6,000,000) a pink coloration only is observed.

In quantitative work the precipitation is made from hot solution and, after standing for about fifteen minutes, the precipitate is filtered in a sintered glass crucible, porosity No. 3, washed with water, dried at 120–130°, and weighed. The nickel furil dioxime complex contains 11·81 per cent. nickel. The reagent is much less soluble in water than in alcohol. A large excess, therefore, is to be avoided and the solution should not stand until cold.

No interference results from the presence of silver. Should copper or zinc be present it is necessary to add ammonium chloride.

Ferric iron, aluminium and chromic salts do not react in solutions containing citrate or tartrate. The use of such reagents enables α-furil dioxime to be employed in the determination of nickel in steels. Ferrous iron must be oxidised since it yields a very sensitive reaction giving rise to a green colour or purple precipitate according to its concentration.

Manganese masks the reaction by producing a precipitate of hydrated dioxide. When this metal is present the solution is best buffered with sodium acetate, the dioxime added, and the mixture neutralised with acetic acid before the oxide appears. When employed in this manner the reagent will detect one part of nickel in 1,000,000 parts of solution and in the presence of at least 1000 parts of manganese.

Cobaltous salts react with α-furil dioxime and give a brown precipitate, but interference may be avoided by oxidising with hydrogen peroxide in presence of ammonium chloride. The test is then carried out with a slight excess of ammonia and will detect one part of nickel in 1,000,000 parts of solution, and in the presence of 1000 parts of cobalt. Since the oxidised cobalt imparts a deep colour to the solution it is necessary to filter if minimal quantities of nickel are present. A red colour may then be observed on the white paper.

α-Furil dioxime has also been employed for the separation of platinum from rhodium, ruthenium, osmium and iridium [2].

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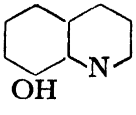
8-HYDROXYQUINOLINE

'Oxine'



Mol. Wt. 145·15

Reagent for Magnesium, Zinc, Aluminium and other metals

8-Hydroxyquinoline is a light buff-coloured crystalline substance, almost insoluble in water but soluble in alcohol, acetone and acids, and melting at 74°–76°. The reagent has been employed in alcoholic solution and in dilute acetic acid. The alcoholic solution is unsuitable for use in the determination of certain metals, notably aluminium, on account of the solvent action of the alcohol on the metal-hydroxyquinoline complex.

8-Hydroxyquinoline forms insoluble co-ordination complexes with many metals. These complexes are of the type $(C_9H_6ON)_2M$, where M is a divalent metal, and are characterised by their definite constitution, their stability and their crystalline, easily filterable form.

Metal ions	In Acetic Acid-Acetate	In Ammoniacal Solution	In Alkaline Solution (NaOH)
Silver ..	Very insensitive	400	No reaction
Mercurous ..	60	20	Precipitation without reagent
Mercuric ..	Insensitive	200	No reaction
Bismuth ..	3	2	Insensitive
Lead	Insensitive	30	Insensitive
Copper ..	1	1	2
Cadmium ..	10	2	3
Cobalt ..	1	20	20
Nickel ..	1	10	20
Aluminium ..	3		
Ferric ..	0·5	10	
Manganese ..	5	1 (NH_4Cl)	Formation of MnO_2
Zinc	1	5	7
Magnesium ..		1	5
Calcium ..		10	

The foregoing table, due to Kolthoff [3], indicates the sensitivity of the reagent in the precipitation of the more common metals. The figures refer to milligrams of metal per litre. Sodium potassium tartrate was added where necessary to prevent precipitation on making alkaline.

General Procedure

The metal is first precipitated with the reagent under the appropriate conditions. Although a considerable number of metals are capable of quantitative precipitation with 8-hydroxyquinoline many convenient separations may be achieved by proper choice of conditions. Much work has been done on the influence of pH on the various precipitations.

The following table summarises the results of Gotô [9, 13], and of Fleck and Ward [8, 15]. The pH range quoted is that range within which complete precipitation was found to occur. Fleck and Ward employed acetate buffers throughout. Gotô normally had tartrate present on the alkaline side.

	Gotô	Fleck & Ward	Others
Copper	2·7 upward	5·33–14·5	
Vanadium	2·7–6·1		
Iron (ic)	2·8–11·2		
Molybdenum	3·3–7·6	3·60–7·33	
Uranium	4·1–8·8		
Aluminium	4·2–9·8		
Cobalt	4·2–11·6	4·33–14·5	
Zinc	4·4 upward	4·58–13·4	
Thorium	4·4–8·8		
Nickel	4·6–10	4·33–14·5	
Titanium	4·8–8·6		
Bismuth	4·8–10·5		
Cadmium	5·4 upward	5·66–14·5	
Manganese	5·9–10		
Magnesium	8·2 upward		
Lead	8·4–12·3		9·3–9·4 [112]
Calcium	9·2 upward		
Tungsten		4·95–5·65	3·3–3·5 [189]

The same authors recorded the pH conditions at which partial precipitation commenced and ceased. Although these results suggest possible separations, a number of which have been put into practice, it must be taken into consideration that co-precipitation of a metal can occur well outside its pH range even of partial precipitation, when another metal is precipitated with 8-hydroxyquinoline in its presence. Thus Moyer and Remington [16] showed that when it is desired to separate zinc from magnesium the former metal must be precipitated at pH 4·6 to 5·5. More alkaline conditions than pH 5·5 cause co-precipitation of magnesium, although precipitation of magnesium from a pure solution of a salt does not commence below pH 7·5.

In spite of these difficulties it is obvious from the table that some metals have exceptional or restricted pH ranges, and should therefore be capable of separation from certain other metals. A number of satisfactory separations have, in fact, been claimed, and some of these are mentioned below under the headings of the particular metals concerned.

Other separations are effected by using tartaric acid, malonic acid or potassium cyanide to hold interfering metals in solution.

The complex having been isolated, a number of methods are available for completion of the analysis. These may be classified as follows:

Gravimetric methods.—(*a*) The precipitate is dried at an appropriate temperature and weighed as the hydrated or anhydrous complex.

(*b*) The precipitate is ignited and weighed as oxide. Certain of the complexes are volatile and must be covered with a layer of anhydrous oxalic acid to prevent loss during ignition.

(*c*) The metal complex is submitted to wet oxidation to destroy the organic matter and the metal determined by a classical procedure.

Volumetric method.—The precipitate is dissolved through the filter with hydrochloric acid and titrated with a standard potassium bromate-bromide solution which quantitatively brominates the 8-hydroxyquinoline to 5 : 7-dibromo-8-hydroxyquinoline. This method is generally to be preferred for accuracy and speed when a number of determinations are to be carried out.

Colorimetric methods.—An approximate method for magnesium depends on measurement of depth of colour due to residual 8-hydroxyquinoline in solution after precipitation of the metal with a standard quantity of the reagent [119].

Teitelbaum [30] and Yoshimatsu [129] treat the precipitated complex with phosphomolybdic acid and sodium tungstate and compare the blue colour developed with standards. A further colorimetric method involves the coupling of the 8-hydroxyquinoline in the redissolved precipitate with diazotised sulphanilic acid or naphthionic acid, the azo dye which is formed being matched against a standard [42, 63, 126, 211]. Yet another method depends upon the formation of a green-blue colour by combination of 8-hydroxyquinoline with ferric ions [109, 147, 158, 159].

Determination of Magnesium

To the solution containing about 0·02 g. Mg in 50 ml. is added sufficient ammonium chloride or acetate to keep the hydroxide in solution, and a few ml. of ammonia in excess. The magnesium is precipitated near the boiling-point with a 2 per cent. solution of 8-hydroxyquinoline in N/1 acetic acid. Excess of the reagent is shown by a yellow colour in the liquid. A large excess is to be avoided on account of the risk of the reagent itself being precipitated. The magnesium compound separates as a yellow crystalline precipitate of the composition $Mg(C_9H_6ON)_2.4H_2O$. The solution is heated to boiling and allowed to stand for about fifteen minutes with occasional stirring. The precipitate is then filtered from the hot solution in a sintered glass crucible, porosity No. 3, and washed with hot weakly ammoniacal water.

The magnesium complex, in common with those of other metals, is inclined to adhere to the sides of the vessel and not to be wetted by the liquid. This property renders it difficult to transfer the precipitate completely to the filter. A trace of sodium taurocholate is effective in reducing this tendency [35] and its employment is an advantage when a gravimetric determination is to follow. For the volumetric method it is not necessary to transfer the precipitate quantitatively since it may be redissolved in the same vessel.

Gravimetric method.—The precipitate is dried at 100°–105°, at which temperature it loses two molecules of water. The weight of the resulting dihydrate × 0·0698 = weight of magnesium. Alternatively a drying temperature of 160° yields the anhydrous complex the weight of which × 0·0778 = weight of magnesium.

Volumetric method.—The precipitate is dissolved through the filter with a little hydrochloric acid of about 5N strength and the filter washed with sufficient water to render the total filtrate about 2N with respect to hydrochloric acid. A little indigo-carmine or methyl red solution is now added and the solution titrated to a yellow colour with M/30 potassium bromate solution.* A few grams of potassium iodide are added and the liberated iodine titrated with N/10 sodium thiosulphate solution using starch solution as indicator.

1 ml. M/30 potassium bromate solution = 0·000608 g. Mg.

(A simple direct titration with bromate solution is not possible since the indicators do not show a sharp end point. Alternatively potassium iodide-starch paper may be used as external indicator, but the back titration is still necessary.)

Solid substances may separate from the solution on addition either of the bromate solution or of the potassium iodide according to the exact conditions obtaining. No inaccuracy results so long as the yellow liquid at the end of the titration is clear or contains only a little yellow silky substance. Occasionally, however, particles of a dark-coloured solid are to be seen and these cause a return of the starch iodide colour, rendering the end point uncertain and inaccurate. This difficulty may be avoided by working with a dilute solution of the complex and avoiding undue excess of bromate. Alternatively 10 to 20 ml. of carbon disulphide may be added before the potassium iodide and the formation of the dark-coloured solid is thus avoided [10].

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* Prepared by dissolving 5·567 g. potassium bromate and 25 g. potassium bromide in water and diluting to 1 litre.

Separation of Magnesium from Calcium

The above method of precipitation separates magnesium from the alkalis and alkaline earths, but in presence of considerable quantities of the latter it is recommended [114] to precipitate the magnesium twice by a somewhat modified procedure as follows.

To the solution containing magnesium and alkaline earths 5–10 g. ammonium acetate and a few ml. of ammonia solution are added. The solution is heated to boiling and the magnesium precipitated with 8-hydroxyquinoline solution as above. To the boiling solution is added more ammonia until the solution is alkaline to phenolphthalein paper. The precipitate is filtered off at once, washed with ammoniacal 5 per cent. ammonium acetate, redissolved in the minimum of hot dilute hydrochloric acid and the precipitation repeated by the same method.

Interference by calcium may also be eliminated by precipitation of this metal with oxalate. The precipitation of magnesium with 8-hydroxyquinoline and the volumetric determination may then be carried through without removal of the calcium oxalate [127]. Magnesium may be determined in presence of fifteen times its quantity of calcium if this technique is adopted. The solution is made to contain about 1 g. of ammonium chloride per 100 ml. and a slight excess of ammonia. It is heated to boiling and sufficient 4 per cent. ammonium oxalate solution added to precipitate the calcium. The precipitate is made granular by heating for about fifteen minutes. The solution is then allowed to cool to about 70° and an excess of 8-hydroxyquinoline solution added, followed by 25 ml. of 5N ammonia. After standing with occasional stirring for fifteen minutes the mixed precipitates are filtered, washed, dissolved in hydrochloric acid and the titration carried out as described above.

Separation of Magnesium from other metals

Precipitation of magnesium from ammoniacal solution effects separation only from alkalis and alkaline earths. Berg [114] claims that precipitation in the presence of 5 g. sodium tartrate and 10 to 20 ml. 2N sodium hydroxide eliminates interference from all heavy metals excepting copper, cadmium and zinc. The 8-hydroxyquinoline is added in the cold and the solution heated to 60° to complete precipitation. We were able to confirm this in respect of aluminium, and Robertshaw [150] notes a practical method for the determination of magnesium in aluminium alloys by precipitation from strongly alkaline solution containing tartrate and cyanide. We found that iron when present in considerable proportion tended to precipitate with the magnesium. By using the maximum proportion of alkali this is minimised and a double precipitation would, no doubt, deal with difficult cases.

A preliminary precipitation of the other metals is often the more successful, or more convenient procedure. Thus Fleck and Ward [8] determine nickel and magnesium in the same solution, both with 8-hydroxyquinoline, by suitable adjustment of pH; zinc and magnesium are dealt with similarly [see also 16] and they suggest the same principle for the separation of molybdenum, cobalt and copper [see also 142], respectively, from magnesium. Also, when little aluminium is present and much magnesium, the former is precipitated first from slightly acid acetate, and then the latter from alkaline solution [23]. An interesting method for the removal of small quantities of iron from the magnesium complex consists in treating it with chloroform in which the iron complex is soluble [157].

Determination of Zinc

The solution should contain about 0·05 g. Zn in 50 ml. and should be slightly acid. Sodium acetate (3–5 g.) is added, the solution warmed to 60°–70° and a 2 per cent. solution of 8-hydroxyquinoline added in excess, as shown by the yellow coloration of the liquid. After warming for a further few minutes the precipitate is filtered on a sintered glass crucible, porosity No. 3, and washed with hot water.

Gravimetric method.—The precipitate (the dihydrate) is dried at 160° to the anhydrous form containing 18·50 per cent. Zn.

Volumetric method.—The procedure described for the volumetric determination of magnesium is followed.

1 ml. M/30 potassium bromate solution = 0·001635 g. Zn.

Separation of Zinc from other metals

The above method separates zinc from the alkaline earths and the alkali metals. If the pH is adjusted to 4·6 to 5·5 magnesium will remain in solution and may be precipitated and determined in the filtrate [8, 16].

Zinc and molybdenum have also been determined in the same solution under controlled conditions of pH [8]. To separate zinc from aluminium the zinc is precipitated from tartrate solution containing sodium hydroxide; the aluminium may be determined in the filtrate by neutralising and making slightly alkaline with ammonia. Cimerman and Wenger [208, 209, 213] have described conditions for the separation of zinc from a large number of other metals.

Determination of Aluminium

The slightly acid solution containing about 0·02 g. Al per 100 ml. is heated to 60°–70° and a 2 per cent. solution of 8-hydroxyquinoline in N/1 acetic acid added in slight excess. A large excess of ammonium acetate is then added above that required to neutralise the mineral acid. The solution is allowed to cool, filtered through a sintered glass crucible, porosity No. 4, and the precipitate washed with water slightly acidified with acetic acid.

Gravimetric method.—The precipitate is dried at 110° and weighed as $Al(C_9H_6ON)_3$ (5·87 per cent. Al).

Volumetric method.—The precipitate is dissolved in a mixture of equal parts of 5N hydrochloric acid and ethyl alcohol (the compound is not readily soluble in aqueous acid), the solution is diluted with about five times its volume of water and the titration carried out as described under Determination of Magnesium.

1 ml. M/30 potassium bromate solution = 0·0004495 g. Al.

Separation of Aluminium from other metals

The method described above separates aluminium from magnesium, the alkaline earths and the alkalis. An alternative method of separation from magnesium is dealt with under that metal. For the determination of aluminium in magnesium alloys Wood [74] recommends preliminary precipitation as hydroxide, while Stenger and others [75] first separate aluminium from most divalent metals by precipitation as benzoate. A considerable amount of attention has been devoted to the separation of aluminium from iron. Berg [98] precipitated the iron with 8-hydroxyquinoline in the presence of tartaric or malonic acid, which was claimed to prevent precipitation of aluminium. The aluminium was afterwards precipitated from the filtrate rendered alkaline with ammonia. Other workers have precipitated iron as oxide [41, 47, 68], or as sulphide [33, 40, 65], or have removed it by electrolysis [59, 60].

Heczko [46] converted iron and other metals into complexes by the use of cyanide, and reduction with hydrogen sulphide. His method has been improved by Fainberg and Tal [61] and by Pigott [70], who has adapted it to the determination of aluminium in ferrous alloys containing a variety of other elements.

Other applications of 8-hydroxyquinoline

The foregoing methods for magnesium, zinc and aluminium represent the departments of analysis in which the reagent has found most useful employment. In the following paragraphs we summarise the available information concerning the determination of other metals. For most of these metals one would not choose to use 8-hydroxyquinoline but the conditions for their precipitation have a direct bearing on the determination of the three main metals in mixtures and should be of interest to the many workers who continue research on this versatile reagent. The table of pH values on p. 77 is of interest in connection with these supplementary notes.

Antimony is precipitated from hydrochloric acid solution by addition of the reagent and subsequent gradual addition of ammonia, as yellow $(C_9H_6ON)_3Sb$. When precipitated from tartrate solution a lighter yellow compound, $(C_9H_7ON)_2.C_9H_6ON.SbO$, is obtained. A gravimetric method has been described [76].

Beryllium is conveniently separated from other metals, particularly aluminium, by precipitating the latter with 8-hydroxyquinoline in acid acetate solution. The precipitate obtained by addition of ammonia to the filtrate contains some 8-hydroxyquinoline, but is of indefinite composition, and is ignited to BeO.

Bismuth. The original method [86] of precipitation as $C_9H_7ON.HBiI_4$ has been found [92] to give low results. Berg's modified method [87] has found more favour and consists in precipitation as $Bi(C_9H_6ON)_3.H_2O$ from acetic acid or ammoniacal solutions free from halides. The complex is dried at 100° and weighed as the monohydrate, or is dehydrated at 140°. Volumetric procedures are also available [92].

Cadmium is precipitated from slightly acid or alkaline solutions as lemon-yellow $Cd(C_9H_6ON)_2.2H_2O$ which is said to yield a lower hydrate (1·5 H_2O) at 100° or the anhydrous compound at 120–130°, but Mitchell and Ward [6] find that the dried compounds are not well defined and recommend the volumetric procedure.

Calcium is precipitated quantitatively, according to Kolthoff [2] from ammoniacal solutions containing much ammonium salts. Barium is not precipitated, but if strontium is present a double precipitation is necessary. Berg [17] states that ammonium salts in any considerable concentration have a solvent effect on the calcium complex.

Chromium in chromic salts yields a greenish yellow precipitate with 8-hydroxyquinoline under a variety of conditions. From alkaline solutions the complex $Cr(C_9H_6ON)_3$ is obtained. The precipitation is not quantitative nor suitable for the accurate determination of chromium, but necessitates special measures in the determination of aluminium with 8-hydroxyquinoline in certain alloys [46, 65]. Chromates yield a precipitate from acetic acid solution. Reduction is said to occur [17, 96] in the hot solution, but the fact that a chocolate brown precipitate is obtained from hot or cold solution suggests that this explanation is at least incomplete.

Cobalt is precipitated from neutral or weakly acid solution. Berg [98] gave the formula $Co(C_9H_6ON)_2.2H_2O$ for the light brown complex and stated that drying at 130° yielded the anhydrous form. Other authors have disagreed with Berg and have either dried to a 1·75 hydrate [99] or recommended the volumetric method [6, 8, 100].

Copper yields yellow $Cu(C_9H_6ON)_2$ and, when precipitated from alkaline tartrate solution, is separated from iron (III), bismuth, arsenic, antimony and tin. The precipitate may be weighed, or dissolved in dilute acid and the copper determined by addition of iodide and titration with thiosulphate. This titration has the advantage that zinc, which precipitates with copper under all conditions, does not affect the result.

Gallium is precipitated from acid solutions by adding 8-hydroxyquinoline in slight excess and then ammonia until neutral or slightly alkaline. Tartrate may be present. The precipitate is dried at 110–150° and weighed as $Ga(C_9H_6ON)_3$ or is titrated with bromate.

Germanium may be precipitated from acid solution containing ammonium molybdate as $(C_9H_7ON)_4.H_4[Ge(Mo_{12}O_{40})]$. The complex is dried and weighed.

Indium is precipitated from acid acetate solution. The precipitate may be dried at 110–120° and weighed as $In(C_9H_6ON)_3$ or titrated with bromate. Precipitation takes place also under more alkaline conditions, but the precipitate is liable to contain $In(OH)_3$.

Iron (III) is precipitated under somewhat exceptionally acid conditions by 8-hydroxyquinoline, and the reagent has, on that account, been found useful in separations involving iron [e.g. 108, 110]. The complex, $Fe(C_9H_6ON)_3$, may be dried at 120° and weighed, or ignited with oxalic acid and weighed as oxide. The volumetric method is also applicable if phosphoric acid is added to prevent interference of ferric ions with the iodine-thiosulphate titration. Ferrey [111] employed this method for pharmaceutical preparations and obtained satisfactory separation from manganese. The complex is of a greenish black colour and its bluish-green tint in organic solvents is the basis of certain colorimetric methods (see p. 78).

Lead is precipitated under alkaline conditions (see p. 77). The method has been used for the gravimetric determination of the metal as $Pb(C_9H_6ON)_2$, but the solubility of the complex is sufficient to render the method rather inexact.

Manganese yields $Mn(C_9H_6ON)_2.2H_2O$ from neutral, ammoniacal or very slightly acid solutions. Generally a mineral acid solution containing excess of the reagent is precipitated by adding ammonia in excess. A darkening of the precipitate through oxidation may be avoided by precipitation in presence of a little sulphur dioxide. Berg [98] found that several hours drying at 110° was necessary to produce an anhydrous complex, and on this account recommended ignition with oxalic acid to Mn_3O_4 or alternatively the usual volumetric procedure. Ferrey [111], on the other hand, claims to obtain the anhydrous complex in one hour at 110° or one and a half hours at 100°.

Molybdenum is precipitated under slightly acid conditions as $MoO_2(C_9H_6ON)_2$ and can readily be separated from those metals which have an alkaline range of precipitation [8]. Fleck and Ward dried the complex at 130° and weighed, stating that it could not be dissolved for volumetric determination [8], but Balanescu [161] employed concentrated sulphuric acid with apparent success. Phosphate does not interfere with molybdenum determinations under the above conditions [12], but in moderately strong acid a phosphomolybdate is formed (see Phosphate below).

Nickel is precipitated over a wide pH range (see p. 77). The yellow complex, $Ni(C_9H_6ON)_2$, is best determined by bromate titration since drying yields an ill-defined hydrate [6, 8].

Niobium. Süe [165] precipitated this metal from neutral oxalate solution and attributed the following approximate formula to the complex dried at 115°, $Nb_2O_5+5{\cdot}5(C_9H_7ON)-4H_2O$. He gave 0·2678 and 0·783 as practical factors for Nb_2O_5 and C_9H_7ON respectively.

Phosphate may be determined by precipitation with 8-hydroxyquinoline in the presence of ammonium molybdate and hydrochloric acid. The conditions are apparently somewhat critical and silica and arsenic are said to interfere [168]. The phosphomolybdate contains 3 molecules of hydroxyquinoline for each atom of phosphorus. Volumetric [166, 169] and gravimetric [168] methods have been devised. On the precipitation of metals in presence of phosphate, see [12].

Rare earth metals are said to be all precipitable by 8-hydroxyquinoline and certain separations have been effected [172, 173].

Silica has been determined by a method similar to that outlined for phosphorus. The complex is given [174] as $SiO_2.12MoO_3.4C_9H_7ON$, which may be weighed, or determined volumetrically with bromate.

Silver is mentioned by Tzinberg [140] as being precipitated quantitatively from ammoniacal solutions, but Kolthoff [3] found the reaction insensitive.

Thorium is precipitated from boiling acid acetate solution as $Th(C_9H_6ON)_4.C_9H_7ON$, which may be air dried and weighed [180].

Titanium yields orange yellow $TiO(C_9H_6ON)_2.2H_2O$ quantitatively from slightly acid or ammoniacal tartrate-acetate titanic solutions. The complex is rendered anhydrous by drying at 110°, or is ignited with oxalic acid to TiO_2, or is dissolved in strong hydrochloric acid and determined by bromate titration.

Tungsten has been determined gravimetrically as $WO_2(C_9H_6ON)_2$, and by ignition of the complex to WO_3, but in view of the narrow pH range (4·95–5·65) given by Fleck [15], and the different and narrower range (3·3–3·5) given by Halberstadt [189], accuracy seems to demand very critical conditions.

Uranium is precipitated as a dark red complex from neutral or slightly acid acetate solutions of uranyl salts. The complex is weighed as $UO_2(C_9H_6ON)_2.C_9H_7ON$ after drying at 110° or is ashed with oxalic acid to U_3O_8, or is determined by the usual volumetric procedure.

Vanadium, as vanadate, gives, from 6 per cent. acetic acid solution, a dark coloured precipitate to which the formula $(C_9H_6ON)_4.V_2O_3$ has been assigned [197]. The complex has been weighed as such [196, 197] and has been determined volumetrically [197] or ignited to V_2O_5. It may be extracted with chloroform from aqueous suspension, the red colour of the extract serving as a sensitive means of detection [197]. Extraction with amyl alcohol [199, 200] is said to provide a more sensitive test suited to colorimetric estimation. Chloroform extraction has also been employed to effect separation from hexavalent chromium [198].

Zirconium nitrate yields a light yellow precipitate from solutions containing excess nitric acid and buffered with acetate. Dried at 130° the complex has the composition $Zr(C_9H_6ON)_4$, and may be weighed as such or ignited to ZrO_2. The volumetric procedure may also be employed. Presence of sulphate or chloride ions leads to the precipitation of complexes of indefinite composition [17].

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See also 3, 6, 9, 12, 16, 19.

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(Separation of other metals in determination of—)

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See 2, 3, 9, 17, 124.

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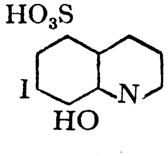
7-IODO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

'FERRON'



Mol. Wt. 351·1

Reagent for Ferric Iron

7-Iodo-8-hydroxyquinoline-5-sulphonic acid is a brown powder, sparingly soluble in water forming a bright yellow solution. When this solution is added to a solution of ferric iron a green or greenish-blue colour develops, which does not fade on standing, and which serves for the detection or colorimetric determination of ferric iron. Ferrous iron does not react with the reagent.

It was noted in earlier editions of this publication that 8-hydroxyquinoline-5-sulphonic acid itself gave similar colours. This has subsequently been reported in the literature [8].

7-Iodo-8-hydroxyquinoline-5-sulphonic acid is employed as a 0·2 per cent. aqueous solution. The solution to be tested is rendered slightly acid, and 0·2 ml. of reagent is added to 50 ml. of solution. The colour reaches its maximum depth within five minutes, and comparison may then be made with standards containing known amounts of ferric iron. The reaction of the solution under test should lie between the limits pH 2 to 4; on either side of this range the sensitivity diminishes. At pH 3 the sensitivity may be given as one part of ferric iron in 5,000,000 parts of solution (this is about half the sensitivity claimed in the literature), whilst a convenient concentration for colorimetric estimation is about 1 in 100,000.

Other metals yielding colourless ions do not interfere, neither do most metals giving coloured ions react with the reagent, although their colour prevents accurate colour matching, and in some cases depresses the sensitivity of the reagent towards ferric iron. The cupric salt of the acid is only slightly soluble, and tends to be precipitated if cupric ions are present. In using the reagent for the colorimetric estimation of ferric iron in the presence of other metals, the user is advised first to investigate its behaviour with mixtures of the pure salts.

The green colour of the ferric-complex assumes a yellowish hue when fluoride is present, and this has been made the basis of a colorimetric determination of fluorine [7].

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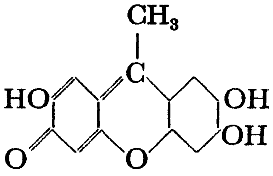
9-METHYL-2:3:7-TRIHYDROXY-6-FLUORONE



Mol. Wt. 258

Reagent for Antimony

The fluorone is a brick-red powder, insoluble in water, soluble in alkali to give a magenta red solution. The reagent is but sparingly soluble in alcohol, and the alcoholic solution shows a yellow green fluorescence. For analytical purposes a 0·1 per cent. solution of the reagent in alcohol containing a few ml. of concentrated sulphuric acid is employed.

Detection of Antimony

Add five to ten drops of the reagent solution to a slightly acid antimony solution containing tartrate. A red precipitate or coloration results according to the concentration of the antimony. The colour contrasts strongly with the lemon-yellow colour of a blank test, and in this way one part of antimony in 5,000,000 parts of solution may be detected.

Under these conditions only a limited number of substances interfere. Titanous, ceric, stannous, arsenic, bismuth, molybdenum, chromous and germanium salts yield similar colours. Tin, arsenic and bismuth do not interfere if the reaction be carried out at pH 4; titanium and chromium when oxidised to their higher valencies with hydrogen peroxide do not react, while cerium compounds do not interfere if reduced to the cerous state by warming with sodium oxalate. Metals giving rise to coloured solutions naturally mask the antimony reaction.

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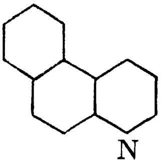
β-NAPHTHOQUINOLINE

(5 : 6-Benzquinoline)



Mol. Wt. = 179·2

Reagent for Cadmium

5 : 6-Benzquinoline is a yellow crystalline powder melting at 93°, soluble in acids and in organic solvents (alcohol, benzene, acetone, ether). The reagent solution is prepared by dissolving 5 g. of the base in 100 ml. of N/1 sulphuric acid, diluting to 200 ml. and filtering if necessary. This reagent when added to a solution containing cadmium forms, in the presence of soluble iodides, a complex of the formula $(C_{13}H_9N)_2H_2CdI_4$ which precipitates as a yellow crystalline solid. Metals which give precipitates with soluble iodides interfere (Cu, Pb, Ag, Sb, Hg and Bi). Ferric ions oxidise the iodide to iodine, but addition of sufficient sulphurous acid prevents this.

Detection of Cadmium

To 10 ml. of the reagent solution are added 5 ml. of 10 per cent. potassium iodide solution and the volume made up to 40 ml. The slightly acid solution to be tested is mixed with an equal volume of this iodide mixture and allowed to stand for a few minutes. The appearance of a yellow turbidity or opalescence indicates the presence of cadmium. Since the reagent mixture when added to water produces an opalescence in a short time, a blank must be prepared. One part of cadmium in 500,000 parts of water may be detected by this reaction.

Determination of Cadmium

The method is dependent upon conditions of precipitation for accuracy [3], and since the complex iodide upon decomposing with ammonia forms a sticky precipitate of the base which tends to occlude iodide, phenyltrimethylammonium iodide (*q.v.*) appears to be a better quantitative reagent for cadmium.

To the solution of cadmium containing sufficient sulphuric acid to produce an acidity of 2N are added 5 grams of sodium potassium tartrate, a little sulphurous acid and about 15 ml. of 10 per cent. potassium iodide solution. To this mixture is added sufficient of the reagent solution to provide an excess of 5 to 6 ml. per total volume of 150 ml. The precipitate is filtered off after one hour on a sintered glass crucible and washed with a solution containing 4 ml. of 10 per cent. potassium iodide, 10 ml. of the β-naphthoquinoline reagent solution and a few drops of sulphurous acid diluted to 100 ml.

The precipitate is then decomposed with ammonia and the resulting iodide treated as described in the monograph on phenyltrimethylammonium iodide.

1 ml. of M/40 potassium iodate = 0·001405 g. Cd.

Interfering metals may be removed by boiling the acid solution with iron for an hour and, after filtering off the excess of iron and precipitated metals, proceeding as described above.

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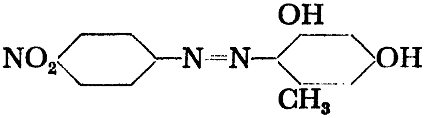
p-NITROBENZENE-AZO-ORCINOL



Mol. Wt. 273·1

Reagent for Beryllium

The reagent is an orange to red powder, sparingly soluble in the usual organic solvents. In analysis the reagent is used as a saturated solution in acetone (0·1 per cent.).

Detection of Beryllium

To 50 ml. test solution add 5 drops of reagent solution and 5 drops of 5N sodium hydroxide. A positive test shows a golden-brown colour, a negative pure yellow.

The concentration limit for detection by this procedure is one part beryllium in a million parts of solution.

By this technique beryllium may be detected in presence of at least 1000 times as much barium, strontium, calcium, arsenic, thallium, vanadate, molybdate and tungstate. By the use of excess sodium hydroxide interference from a similar preponderance of either aluminium, tin or lead may be removed.

In presence of potassium cyanide, a like excess of either zinc, cadmium, silver, mercury, nickel or copper does not interfere.

In presence of antimony, bismuth or manganese, beryllium gives a positive test if solution is maintained by the use of potassium citrate or sodium potassium tartrate.

Magnesium, iron, chromium and cobalt in similar excess interfere.

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p-NITROBENZENE-AZO-RESORCINOL

'MAGNESON I'

AND

p-NITROBENZENE-AZO-α-NAPHTHOL

'MAGNESON II'

and other Reagents for Magnesium

The first of the above-named dyes was proposed in 1926 [1] as a reagent for magnesium. The second was subsequently found to possess a higher degree of sensitivity for the same purpose. Since it appeared that the property of giving distinctive colours with magnesium was characteristic of dyestuffs in which *p*-nitraniline, after diazotisation, was coupled with phenols, a number of such compounds were prepared in this laboratory, and critically examined as reagents for magnesium. The substances prepared are listed below in ascending order of efficiency, the colours given with a magnesium concentration of 20 parts per million of solution being stated.

Coupling with	Colour of +ve Test	Blank	Sensitivity at 2 in 10^6 of Mg
α-Naphthol	Bright blue	Purple	Excellent
Salicyl sulphonic acid	Violet	Pink	V. Good
1-Naphthol-2-sulphonic acid	Bright blue	Mauve	V. Good
β-Naphthol	Blue	Pink	V. Good
1·3-Xylen-4-ol	Blue	Red	V. Good
Resorcinol	Blue	Red-Violet	Good
Phloroglucinol	Pink	Yellow	Good
Vanillin	Violet	Pink	Good
Phenol	Mauve	Orange	Good
Orcinol	Light brown	Yellow	Good

Detection of Magnesium

All the reagents were used as 0·1 per cent. solutions in 1 per cent. sodium hydroxide.

To the slightly acid test solution was added three drops of reagent solution, followed by excess 5N sodium hydroxide. The sensitivities of the reagents varied from detecting at one part in 5,000,000 parts of solution (α-naphthol compound) to one part in 1,000,000 parts of solution (resorcinol compound).

Metallic Interference

Using *p*-nitrobenzene-azo-α-naphthol, magnesium could be detected in a concentration of two parts per million in the presence of 1000 times as much calcium, barium, strontium, arsenic, antimony (using sodium citrate and a blank test), lead, and after addition of sufficient cyanide, silver, copper, cadmium, mercury, and zinc.

Large excesses of iron, chromium, and cobalt gave colours masking the test, while bismuth, tin, aluminium, titanium, nickel and beryllium interfered. Ammonium salts impaired the sensitivity of the reagents, and tartrates, but not citrates or oxalates, inhibited the reaction.

This latter fact could quite easily be made the basis of a confirmatory test for tartrates.

It is evident from the above remarks on metallic interference that generally the most expedient procedure is to precipitate all metals up to and including the zinc group, to volatilise ammonium salts and apply the test to the residue.

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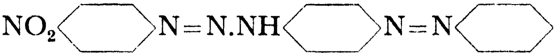
p-NITROBENZENEDIAZOAMINOAZOBENZENE

‘ CADION ’



Mol. Wt. 346

Reagent for Cadmium, Magnesium, Mercury and Bismuth

This reagent, for which the trivial name Cadion has been suggested, is a red-brown powder, insoluble in water or acids, slightly soluble in alcohol, and readily soluble in alcoholic alkalis. With alkaline cadmium solutions containing alcohol the reagent gives a pink colour, magnesium under the same conditions producing a blue coloration. The colour of the reagent in acid mercurial solutions is unchanged on adding excess alkali, remaining yellow. This yellow colour reverts to the normal mauve colour of a blank test on the addition of cyanide.

The reagent is employed as a 0·05 per cent. solution in acetone.

Detection of Cadmium

To the neutral or slightly acid test solution are added four drops of reagent solution followed by excess of normal alcoholic potassium hydroxide. A solution containing only one part of cadmium per 100,000,000 parts of solution will give a positive reaction.

The pink colour given is discharged on the addition of cyanide.

Metallic Interference

Using the procedure described above, cadmium may be detected in the presence of 10,000 times as much bismuth, lead, tin, arsenic, antimony, aluminium, zinc, calcium, strontium, barium, beryllium, or the alkali metals although in several of these combinations it is advisable to perform a blank experiment. Magnesium interferes badly, however, and should be removed.

Detection of Magnesium

To the acetic acid solution of magnesium are added four drops of the reagent solution followed by excess of normal potassium hydroxide. With no other metals present the reagent gives a blue coloration at a concentration of two parts in 1,000,000, and a mauve colour down to one part in 5,000,000 of solution.

Metallic Interference

The addition of cyanide will remove interference from zinc, cadmium, mercury, copper and from small amounts of nickel.

Beryllium, aluminium, tin and most highly coloured ions interfere badly and should be separated.

Detection of Mercury

Under the same experimental conditions as stated above, and in the absence of cyanide, mercury may be detected in a concentration of one part in 20,000,000 parts of solution.

Metallic Interference

Mercury may be detected in the presence of 10,000 times as much magnesium, 5000 times as much cadmium, provided in the latter case that sodium potassium tartrate be employed. Tin interferes at all concentrations and should be removed. Other metals do not appreciably interfere.

Use as a confirmatory test for Bismuth

If to a bismuth solution containing more than 0·5 per cent. Bi, be added four drops of reagent solution followed by excess normal potassium hydroxide, a sky-blue colour forms on the precipitate. With weaker bismuth solutions, the blue colour appears upon using stronger potash.

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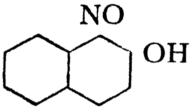
α-NITROSO-β-NAPHTHOL



Mol. Wt. 173·2

Reagent for Cobalt, Iron and Copper

α-Nitroso-β-naphthol is a brown powder melting at 109°. It is insoluble in water, but dissolves in alcohol, acetic acid and benzene. For the detection of metals a saturated solution in 50 per cent. acetic acid is used, and this solution is best prepared by dissolving 10 g. of the solid in 500 ml. of the diluted acid with the aid of heat. When cold the solution is filtered from excess of the reagent.

α-Nitroso-β-naphthol when added in excess to neutral or slightly acid solutions of cobalt, copper, palladium or ferric salts precipitates the metal completely. Tin, silver, chromium, uranium and bismuth are also precipitated but not quantitatively, whilst mercury, lead, cadmium, arsenic, antimony, aluminium, beryllium, manganese, nickel, calcium, magnesium and the alkali metals remain in solution.

Detection of Cobalt by the Spot-reaction [8, 17, 18]

The neutral, or slightly acid solution to be examined is dropped on to a filter paper, and a drop of α-nitroso-β-naphthol solution (1 g. in 50 ml. acetic acid diluted to 100 ml.) is allowed to fall on to the previous spot. Cobalt is indicated by the appearance of a brown spot. One part of cobalt in 1,000,000 can be detected in this way. Modified methods allow cobalt to be detected in the presence of iron, copper and uranium [18].

Determination of Cobalt, Iron and Copper

The metal in solution, preferably as chloride, is rendered free from the other metals which give precipitates with α-nitroso-β-naphthol, by means of the ordinary group reactions, and is then diluted so that not more than 0·1 g. is present in each 50 ml. of solution. The solution is neutralised with ammonia and then made faintly acid with hydrochloric acid. After heating to boiling 100 ml. of the reagent solution are added for each 0·1 g. of cobalt (or other metal) and heating with stirring is continued for a few minutes. The hot solution is allowed to stand for two hours, the precipitate is then filtered off, washed with water, dried, and ignited.

The cobalt complex may be ignited in three ways:—

(*a*) in a stream of hydrogen.	Weighed as	Co.
(*b*) in a stream of carbon dioxide.	,,	CoO.
(*c*) in a stream of air or oxygen.	,,	Co_3O_4.

The last method is recommended.

The copper complex is ignited in an open crucible and weighed as CuO and the iron complex is treated similarly and weighed as Fe_2O_3.

The precipitates contain α-nitroso-β-naphthol in excess of the amount required to combine with the metal and are thus of indefinite composition and cannot be weighed with accurate quantitative results. It is claimed that the complex produced from cobaltic salts and α-nitroso-β-naphthol is of definite composition [14, 31]. Owing to the extremely bulky nature of the complexes, it is not desirable to use more than 0·1 to 0·2 g. of metal in each determination.

Iron and cobalt may be precipitated together, ignited and weighed and the iron then estimated in another sample by precipitation with ammonia.

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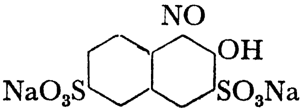
NITROSO-R-SALT



Mol. Wt. 377·3

Reagent for Cobalt and Iron

This compound is at present supplied as the free acid, a dark yellow powder giving a green solution in alkaline media. With cobalt salts in alkaline solution a deep red colour is produced which is not dispersed on acidification.

Detection of Cobalt

To the cobalt solution (50 ml.) contained in a Nessler cylinder are added 1 g. of sodium acetate and 3 drops of a 0·5 per cent. solution of the reagent in water. The solution if not faintly alkaline should be made so by the addition of 5N sodium hydroxide. Cobalt may be detected by this method if present in a concentration of one or more parts per 30,000,000 of solution.

Metallic Interference

By the use of the method above, cobalt may be detected even when accompanied by 1000 times as much zinc (using KCN), magnesium, copper (using KCN), cadmium, mercury (KCN), aluminium, lead, bismuth (using citric acid), silver, beryllium, arsenic, antimony (using sodium potassium tartrate), strontium, calcium, barium, manganese, thallium, ammonia, the alkali metals, and iron (using sodium citrate with no sodium acetate and performing a blank test).

Tin and titanium interfere with the detection and should be removed.

Nickel, when present more than 100 times in excess of the cobalt, should be precipitated by dimethylglyoxime and the reagent solution added to the filtrate.

The reagent has also been used indirectly to determine potassium by estimating colorimetrically the cobalt content of the precipitated potassium cobaltinitrite [5, 16].

Detection and Determination of Iron

The reagent gives with solutions of ferrous salts (reduction of ferric is easily achieved by means of hydroxylamine salts) buffered at a pH of 8 to 10, an intense green colour, the strength of which is proportional to the iron content. The buffer employed [15] is sodium acetate, although ammonium hydroxide may be used to achieve the required alkalinity.

The sensitivity reported by Sideris is one part in 5,000,000 parts of solution.

The detailed procedure is as follows:—To 10 ml. of neutral test solution add 1 ml. hydroxylamine sulphate solution (10 per cent. *w/v* in water), 1 ml. of reagent solution (0·5 per cent. in a mixture of 70 ml. water and 30 ml. acetone), and 2 ml. sodium acetate solution (54 per cent *w/v* in water).

Make up to 15 ml., allow to stand for twenty minutes or more and either compare with simultaneously prepared standards or determine in a photoelectric colorimeter and read off on a calibrated graph.

Determination of Cobalt

Much attention has been given in recent years to the determination of small amounts of cobalt in plants and soils in view of its lately discovered connection with "bush sickness" and other diseases of cattle and sheep, mostly by New Zealand chemists.

Various methods have been employed and chemists concerned with this and like problems should consult the original literature.

To determine cobalt after the destruction of organic matter, proceed as follows:—

To 5 ml. of neutral test solution add 1 g. sodium acetate and 1 ml. reagent solution. Boil gently for two minutes, add slowly 1 ml. nitric acid (s.g. 1·42), and boil for a further one minute. Make up to 10 ml. with water, filter if necessary, and match with standards simultaneously prepared or read off in a Lovibond tintometer and check with a calibrated graph.

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PHENYLTHIOHYDANTOIC ACID

$C_9H_{10}O_2N_2S$

Mol. Wt. 210·2

Reagent for Cobalt and Antimony

Phenylthiohydantoic acid is a white crystalline substance melting at about 157°. It is soluble in hot water and hot alcohol.

From a dilute solution containing citric acid and made alkaline with ammonia, cobalt is quantitatively precipitated as a reddish-brown complex of tea-leaf appearance, which filters easily with suction and on ignition passes to impure Co_3O_4.

The reagent will free nickel solutions of cobalt but some nickel is always co-precipitated.

Gravimetric Determination of Cobalt

To 400 ml. of a solution containing not more than 25 mg. cobalt, 7 g. of citric acid are added, followed by sufficient ammonia solution to render the liquid fairly alkaline to phenolphthalein.

About 0·8 g. of the reagent dissolved in 30 ml. of hot alcohol is added with stirring, and the whole boiled for a short time. When precipitation is complete the supernatant liquor may still be red in colour but this colour is adsorbed on the precipitate when filtered.

The method we have employed to evaluate this precipitate is to heat with concentrated sulphuric acid and hydrogen peroxide, weighing as $CoSO_4$, which contains 38·03 per cent. of Co.

The reagent employed in this manner will completely separate cobalt from manganese, and also, according to Willard and Hall [2], from arsenic, zinc, titanium, uranium, vanadium, tungsten, molybdenum, aluminium, chromium, calcium and magnesium in one precipitation. In our experience, however, the separation from zinc requires at least a double precipitation.

Separation of Antimony

Lassieur [3] separated antimony from arsenic by precipitation with the reagent from acetic acid solution, the complex, after drying in a desiccator, containing 18·7 per cent. Sb.

Other metals precipitated from acetic acid solution are copper, lead, mercury, cadmium and bismuth.

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PHENYLTRIMETHYLAMMONIUM IODIDE

$C_6H_5(CH_3)_3NI$

Mol. Wt. 263·1

Reagent for Cadmium

Phenyltrimethylammonium iodide is a white or pale yellow crystalline compound which is soluble in water, alcohol, and, to a lesser degree, in benzene and chloroform. It is used as a selective reagent for cadmium, for which purpose a 2·5 per cent. aqueous solution is employed. In the presence of potassium iodide phenyltrimethylammonium iodide forms a white crystalline precipitate with cadmium. The precipitate has the formula $[C_6H_5(CH_3)_3N]_2CdI_4$, and separates in needle-like crystals.

Detection of Cadmium

To 10 ml. of the neutral or slightly acid solution to be tested are added 5 ml. of 10 per cent. potassium iodide solution and 5 ml. of phenyltrimethylammonium iodide solution. In the absence of metals which give precipitates with soluble iodides (Cu, Pb, Ag, Sb, Hg and Bi) a white crystalline precipitate is formed if cadmium be present. Scratching the side of the test tube may be necessary to facilitate the precipitation when only traces of cadmium are present. One part of cadmium may be detected in 40,000 parts of water by this means. The following ions are unaffected by the reagent under the conditions of the experiment: stannous, arsenious, chromic, aluminium, ferrous, manganous, nickel, cobalt, zinc, calcium, strontium, barium and magnesium. Ferric ions oxidise the iodide to iodine, but addition of sufficient sulphurous acid solution prevents this.

Determination of Cadmium [1]

Other group II metals are removed by making the solution 2N with respect to sulphuric acid and heating the solution just below the boiling-point with metallic iron. After one hour the metallic precipitate is filtered on a sintered glass crucible and to the filtrate and washings are added a few drops of sulphurous acid solution, 5 g. of sodium potassium tartrate, 3 g. of potassium iodide and 30 ml. of the reagent solution. The crystalline cadmium complex is filtered, after standing for six hours, on a sintered glass crucible (No. 4) and washed with successive quantities (5 ml.) of a solution containing 1 g. potassium iodide and 1 g. phenyltrimethylammonium iodide in 200 ml. of water. The precipitate is dissolved in about 20 ml. of 2N ammonia solution in the glass crucible and the solution drawn through into a suitable vessel. The filtrate and washings are transferred to a flask and titrated with M/40 potassium iodate as follows. The ammoniacal solution is neutralised and then an equal bulk of 2N hydrochloric acid is added. Five ml. of potassium cyanide (10 per cent.) are then added and starch solution. The iodate is run in until the blue colour first formed changes to violet and finally becomes colourless.

$$1 \text{ ml. } M/40 \ KIO_3 = 0{\cdot}001405 \text{ g. Cd.}$$

Up to 50 mg. of cadmium in the presence of as much as 1 g. of zinc may be determined in this way, and if lead, tin, copper, bismuth, antimony and arsenic also are present they may be removed by the use of metallic iron as described above.

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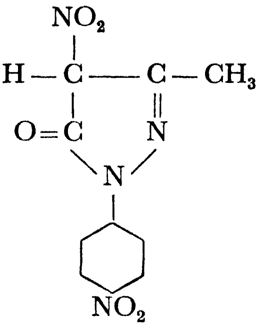
PICROLONIC ACID

(1-*p*-Nitrophenyl-3-methyl-4-nitro-pyrazolone-5)



Mol. Wt. 264·2

Reagent for Copper, Lead, Calcium and Thorium

Picrolonic acid is a yellow crystalline powder which melts at 125° with decomposition. It dissolves in alcohol and in water to form a clear yellow solution, and it has been used to identify organic bases and as a reagent for the detection of copper, lead, calcium and thorium. With calcium the picrolonate has the composition $Ca(C_{10}H_7N_4O_5)_2.8H_2O$ and if carefully dried can be weighed conforming to this formula. Other metals of the calcium group give crystalline precipitates with picrolonic acid which are more soluble than the calcium salt, but it has been stated that there is considerable chance of contamination of the calcium precipitate with picrolonates of elements of the same group [3].

Lead picrolonate is precipitated quantitatively from neutral solutions and has the formula $Pb(C_{10}H_7N_4O_5)_2.1{\cdot}5H_2O$.

Detection of Copper, Lead, Calcium and Thorium

To 10 ml. of the neutral solution to be tested an equal volume of picrolonic acid solution (2·5 g. per litre) is added. A yellow precipitate or turbidity is produced by each metal. If the concentration is low, calcium and lead picrolonates do not appear immediately, and with very small concentrations the solution may remain clear for several hours. Stirring accelerates the precipitation.

The sensitivities of these reactions are approximately:—

Calcium	one part in 1,000,000
Lead	,, 500,000
Thorium	,, 500,000
Copper	,, 300,000

Identification of Organic Bases

The usual method is to dissolve the base in alcohol and to add an alcoholic solution of picrolonic acid in approximately equivalent amount. The precipitated salt is filtered off and recrystallised. The picrolonates are very well crystallisable substances with definite melting points.

A valuable method of converting a picrate into a picrolonate has been described [4].

Determination of Calcium

(*a*) *Gravimetric*.—The solution should be neutral to litmus and free from the other metals which give precipitates with picrolonic acid. Magnesium and the alkalis may be present in quantity up to ten times the amount of calcium present without affecting the accuracy of the results. Not more than 0·1 g. of calcium should be precipitated and for this amount 2 g. of picrolonic acid should be dissolved in 750 ml. of hot water and added to the hot solution of the calcium salt.

The precipitate is at first flocculent but later becomes crystalline. After standing for several hours (preferably over night) the precipitate is filtered on a tared No. 3 sintered glass crucible, washed with a little water and dried to constant weight by drawing air through it on the filter pump. The calcium picrolonate is usually dry within two hours, and for accurate work it is desirable to filter the air through a cotton wool plug.

$$\text{Wt. of precipitate} \times 0{\cdot}05642 = \text{Wt. of Ca.}$$

Calcium may be separated from magnesium by the above procedure provided the concentration of magnesium is not more than ten times that of the calcium. The magnesium may be estimated in the filtrate by adding a considerable quantity of alcohol and then sodium phosphate and ammonia as usual. A small amount of picrolonate occurs in the precipitate but disappears on ignition. The method may be used to estimate the hardness of water [2].

(*b*) *Colorimetric.*—A rapid colorimetric method for the determination of calcium has been developed [5]. The precipitate of calcium picrolonate is filtered off and adhering liquid is washed away by means of ether. The calcium salt is then dissolved in hot water and 1 ml. of saturated aqueous bromine solution added (for 50 ml. of solution). The mixture is heated in a water-bath for ten minutes, 10 ml. of alcohol added, and the mixture cooled. The addition of 2 ml. of 2N sodium hydroxide results in a pink solution which is compared in a colorimeter with solutions containing known quantities of picrolonate.

Determination of Lead [6]

The solution, containing 0·1 g. lead, should be neutral and should contain no more than traces of alkali metal or ammonium salts. The addition of picrolonic acid solution (2·5 g. per litre) is made at the boiling-point and slow addition produces an easily filterable crystalline precipitate. A total volume of 150 ml. of the acid is used. After cooling to about 0° in ice, the precipitate is filtered off on a No. 3 sintered glass crucible, washed with a small quantity of ice-cold water and dried at 130° to 140°.

$$\text{Wt. of precipitate} \times 0{\cdot}2725 = \text{Wt. of Pb.}$$

Determination of Thorium [10]

A method has been described for the quantitative estimation of thorium with picrolonic acid. The precipitation must be made from boiling solution, but even so the thorium picrolonate is of a colloidal nature and is difficult to filter. The method offers no advantages over existing procedures and at the same time is more restricted in its use.

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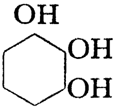
PYROGALLOL



Mol. Wt. 126·1

Reagent for Antimony, Bismuth, Titanium, Copper, Iron, other metals and Iodate

Pyrogallol is a white crystalline substance melting at 133°, easily soluble in water and most organic solvents.

Detection of Antimony

Antimony in dilute acid solution gives an insoluble pyrogallate, serving as a selective test for the metal. The precipitate is crystalline and may be used as a means of detecting antimony by spotting the acid test solution on a microscope slide and slowly adding an aqueous solution of the reagent. Characteristic crystals of the antimony compound may be observed under the microscope.

Determination of Bismuth

The bismuth solution, acidified with dilute nitric acid, is boiled and a slight excess of an aqueous solution of pyrogallol added (about 0·07 g. of reagent per 0·1 g. Bi), followed by ammonia solution until the solution (200 ml.) is alkaline to litmus. Dilute nitric acid is added until the solution is just acid to the same indicator. The yellow granular precipitate is left to settle and then filtered through a tared Gooch crucible, washed with 1 per cent. nitric acid and water. After drying at 110° for twenty minutes, the crucible is cooled and weighed, the dried precipitate containing 62·95 per cent. of Bi.

Feigl and Ordelt [7] separate bismuth from lead in this manner, precipitating the lead in the filtrate as sulphide, filtering and oxidising to sulphate.

Detection and Determination of Molybdenum

When an aqueous solution of the reagent is added to a neutral solution of a molybdate a cherry-red coloration is produced. For the colorimetric determination of molybdenum the neutral test solution is diluted to a concentration of 5–10 mg. Mo per 100 ml.

To 10 ml. of this solution add 10 ml. 1 per cent. solution of pyrogallol in 2 per cent. acetic acid, and 10 ml. of fifth-normal sodium acetate solution. The coloration developing is compared with standards similarly prepared.

Detection of Osmium [18]

The reference quoted states that if to a solution containing sodium osmate is added a drop of hydrochloric acid followed by a drop of concentrated aqueous pyrogallol solution, a blue colour is given even if the concentration of osmium is as little as 0·01 mg. per ml.

Rhodium and iridium do not interfere but palladium and platinum give a brown, and gold a purple colour.

Detection of Titanium

The reagent is employed as a 2 per cent. solution in saturated aqueous sodium sulphite solution. Addition of one drop to the test solution will give a yellow or orange colour if titanium is present in a concentration of one part or more per 10,000,000 parts of solution.

Detection and Determination of Iron

The reagent, employed as above, gives with iron solutions when neutral, a blue-violet colour. This reaction is sensitive to an iron concentration of one part in 5,000,000 parts of solution. The colour given is proportional to the iron present and the test solution may thus be compared with freshly made standards.

The blue colour given changes to red on making the solution faintly ammoniacal.

Detection of Copper

The reagent, again employed as above, gives a red coloration in neutral copper solutions. This detection is sensitive to one part of Cu in 1,000,000 parts of solution.

Separation and Determination of other metals

The reagent (used as a 5 per cent. aqueous solution) will separate niobium and tantalum from titanium and zirconium in approximately N/1 hydrochloric acid.

Niobium gives a yellow coloration with alkaline, but not acid solutions of the reagent in aqueous sodium sulphite, the reverse being the case for tantalum. This can be made the basis of colorimetric determination of both niobium and tantalum.

Pyrogallol prevents the precipitation of $Al(OH)_3$ and liberates an equivalent amount of acid from aluminium salts, according to the equation:—$Al^{\cdot\cdot\cdot}+C_6H_3(OH)_3=3H^{\cdot}+C_6H_3O_3Al$.

Aluminium may be determined by titrating the free acid formed by electrometric titration, after the addition of 3 per cent. aqueous reagent solution.

Detection of Iodate

An acid solution of the reagent yields a red colour with iodates, and iodate may thus be detected even in the presence, according to Gottlieb [21], of perchlorate, chlorate, thiosulphate, bromate, silicofluoride, permanganate or bromide.

Iodide and chromate, however, interfere.

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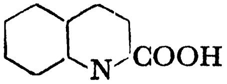
QUINALDINIC ACID



Mol. Wt. 173·2

Reagent for Copper, Zinc, Cadmium and Iron

Quinaldinic acid is a yellowish crystalline powder melting at 155–157° which is practically insoluble in cold water, readily soluble in hot. The reagent readily dissolves in caustic soda and ammonia to form sodium and ammonium quinaldinates.

Quinaldinic acid forms salts of definite composition with mercury, lead, silver, cadmium, zinc, nickel and cobalt, and basic salts with iron, uranium, aluminium and chromium. The copper, cadmium and zinc salts can be quantitatively precipitated from dilute acetic acid solutions as well as from neutral solution. Uranium forms a golden insoluble amorphous precipitate which is soluble in acids. Ferric salts give an amorphous yellow precipitate which is somewhat soluble in mineral acid solution; chromium and aluminium behave similarly. In contrast with ferric salts, ferrous salts give a dark red flocculent precipitate which rapidly changes to a violet colour. Traces of ferrous iron give a pale red colour with the reagent; the colour is intensified by the addition of potassium cyanide and this can be made the basis of a colorimetric estimation of iron.

Determination of Copper [1]

The reagent solution is prepared by neutralising 5 g. quinaldinic acid with caustic soda and diluting to 150 ml.

To the boiling copper solution, acidified with acetic acid and diluted to about 150 ml., is added a slight excess of the reagent when the green copper quinaldinate precipitates. This is filtered off on a No. 4 porous crucible, washed with hot water and dried to constant weight at 125°. The precipitate, which has the formula $(C_{10}H_6NO_2)_2Cu.H_2O$, contains 14·96 per cent. Cu. Adopting this procedure copper can be separated from lead, phosphate, arsenate and arsenic.

Determination of Cadmium [1]

Cadmium can be precipitated from neutral or slightly acid solution, the solution being finally made neutral with ammonia. The precipitation is made from a hot solution, allowed to cool and filtered through a sintered crucible porosity No. 4. The precipitate is washed with cold water and dried at 125°. The cadmium salt has the composition $(C_{10}H_6NO_2)_2Cd$ containing 24·63 per cent. Cd.

Determination of Zinc [1]

The zinc can be precipitated from a dilute acetic acid solution and is determined in a manner similar to that described for copper. The zinc quinaldinate has the formula $(C_{10}H_6NO_2)_2Zn\,.\,H_2O$ corresponding to 15·29 per cent. Zn.

The reagent offers a really useful estimation of zinc in the presence of manganese, magnesium, barium, strontium, iron, aluminium, beryllium, titanium and uranium providing the conditions stated below are strictly adhered to [2].

The solution is boiled with a few drops of nitric acid to oxidise any ferrous iron to the ferric state. The solution is cooled, 4–5 g. sodium potassium tartrate are added, followed by 4–5 g. ammonium chloride. Two drops of 0·02 per cent. methyl red and two drops of methylene blue of the same concentration are added and the solution is neutralised with ammonia. The methylene blue—methyl red indicator changes from violet-blue to green as the pH alters from acid to alkaline. The colour change of the mixed indicator is sharper than that of methyl red alone. One drop of 2N ammonia is added in excess and the whole diluted to a bulk of 150–160 ml. and heated to 50°. The sodium quinaldinate reagent is added dropwise, with constant stirring, in slight excess and the precipitate allowed to settle. It is essential the solution should not contain excess of ammonia for zinc quinaldinate is soluble in ammoniacal solution. The precipitate is filtered on a sintered crucible, washed with hot water and dried at 125°. The precipitate is usually a pale blue tint due presumably to adsorption of methylene blue but this in no way affects the accuracy of the method.

The reagent can also be employed for the estimation of zinc in the presence of cuprous, mercuric and silver ions [12]. To the nearly neutral solution, diluted to 200 to 300 ml., is added 8 g. potassium iodide, 5 ml. dilute acetic acid, a freshly prepared solution containing 6 g. sodium bisulphite and a solution of 6 g. thiourea. The clear solution is brought to the boil, sodium quinaldinate is added, and the zinc precipitate is filtered off, washed and dried as described above.

Colorimetric Determination of Iron [1]

For the colorimetric detection of iron the reagents are added to the solution under test in the sequence named:—1 ml. 5 per cent. hydroxylamine hydrochloride solution, 1 ml. sodium quinaldinate reagent and 1 ml. 10 per cent. potassium cyanide solution. A red colour develops when iron is present and the sensitivity of the reaction is one part in 14,000,000 parts of solution.

For the quantitative estimation a known volume of the solution to be tested is taken and the colour, produced as previously described, is compared with that produced by a standard iron solution. On long standing, particularly at high temperatures, the colour fades, hence the solutions must be kept at room temperature. Metals which give precipitates with quinaldinic acid interfere to some extent with the colorimetric estimation and, in general, lower the sensitivity of the reagent.

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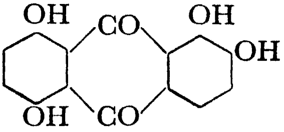
QUINALIZARIN

(1 : 2 : 5 : 8-Tetrahydroxyanthraquinone)



Mol. Wt. 272·2

Reagent for Beryllium, Magnesium, Aluminium and Borate

Quinalizarin is a dye which dissolves in alkalis to form a violet-coloured solution turned yellow by addition of acid. The addition of the alkaline solution to an alkaline solution of a beryllium or magnesium salt produces a blue colour, and this reaction may be used to detect minute quantities of these metals (beryllium in a concentration of 1 : 2,000,000, or magnesium in a concentration of 1 : 1,000,000), the reaction being carried out in presence of sodium hydroxide. Greater sensitivities are obtained by substituting a 10 per cent. solution of ethylene diamine in alcohol for sodium hydroxide solution [22]. When it is required to detect beryllium in the presence of magnesium, ammonium chloride is added to the solution which is then rendered alkaline with ammonia. Quinalizarin then produces a colour with both metals but on addition of bromine water the magnesium compound and the excess dye are decomposed whilst the beryllium compound remains. The use of ammonia in this technique lowers the sensitivity to about one third of the figure given above.

Aluminium does not interfere provided sufficient concentration of sodium hydroxide is present, but if tartrate is also present a violet colour is formed which causes interference. Small quantities of iron do not interfere if tartrate be added. Lead, zinc, tin and phosphate have no influence, and solutions containing copper, nickel or cobalt may be decolorised with cyanide. Zirconium, cerium and thorium, as well as certain other metals of the rare earths, are stated [16] to give the same reaction as beryllium, including the stability of the coloured compounds in presence of bromine.

In slightly acid solution aluminium forms a reddish violet colour as distinct from the yellow colour given by the dye alone or the dye in presence of magnesium. This reaction provides a delicate test for aluminium.

Detection of Beryllium

A 0·05 per cent. solution of quinalizarin in N/4 sodium hydroxide solution is employed. This solution is somewhat unstable and should be freshly prepared on the day it is used. Ten ml. of the solution to be tested are mixed with a few drops of the reagent, the solution is rendered alkaline by the addition of 5 ml. of N/1 sodium hydroxide solution and the resulting colour compared with a blank containing 10 ml. of water and similar amounts of quinalizarin and sodium hydroxide. With concentrations of beryllium down to 1 : 2,000,000 the test is found to be distinctly more blue than the blank. When aluminium is present a greater concentration of sodium hydroxide may be required to retain aluminium hydroxide in solution; in this case the blank must contain a similar concentration of the alkali since its colour is to some extent dependent on this factor.

Detection of Beryllium in presence of Magnesium

The solution, if acid, is neutralised with ammonia and to 10 ml. 1 g. of ammonium chloride is added followed by 2 ml. of 5N ammonia and a few drops of the reagent. A violet colour now develops if beryllium and mangesium are present. If 5 ml. of saturated bromine water are now added slowly with shaking the violet colour of the solution fades at once, the colour due to magnesium and the excess quinalizarin being destroyed. If beryllium is present a blue colour remains but the beryllium compound rapidly separates as a blue precipitate leaving the liquid colourless. If the test is allowed to stand for several hours the precipitate may be more clearly observed at the bottom of vessel and in this way one part of beryllium in 650,000 may be detected in presence of a considerable quantity of magnesium.

Colorimetric Determination of Beryllium

Fischer's method for approximate estimation of beryllium is described in detail by Mitchell and Ward [12].

Detection of Magnesium

This is carried out in a manner similar to that described for beryllium, the sensitivity being 1 in 1,000,000. This sensitivity is adversely affected by ammonium salts which should therefore be eliminated.

Detection of Beryllium and Magnesium by the Drop-reaction

The technique for the drop-reaction is described by Feigl [11]. It is found, however, that the procedure recommended for detection of beryllium in presence of magnesium results in complete decolorisation even when beryllium is present. It is more satisfactory to follow the principle of the technique described above—one drop of the solution is mixed with one drop of ammonium chloride solution (1 : 5) and two drops of 0·05 per cent. quinalizarin solution in N/4 sodium hydroxide. The further addition of 1–2 drops one-fifth saturated bromine water destroys the colour due to magnesium and excess quinalizarin.

Detection of Aluminium in presence of Magnesium

The solution to be tested is mixed with sufficient quinalizarin solution to impart a definite tint and is made slightly alkaline (blue violet colour) with dilute sodium hydroxide solution. The solution is then boiled, allowed to stand a few minutes and cooled. Dilute acetic acid is added until the colour changes. In the absence of aluminium a yellow colour is obtained. Aluminium produces a reddish-violet shade.

The reaction may also be carried out as a spot test on paper moistened with quinalizarin solution. The moist spot is made alkaline with the vapour from a bottle containing ammonia, then, on acidifying in a similar manner over a bottle of acetic acid, aluminium is indicated by a reddish-violet colour.

A solution of quinalizarin in aqueous pyridine is recommended [14] for the test-tube technique and a solution in acetone and a little pyridine for the spot technique. We find, however, that a solution in very dilute sodium hydroxide solution serves quite well in both cases.

Determination of Aluminium [4]

To 10 ml. test solution, neutral in reaction, add 0·25–0·3 ml. of a 1·0 per cent. solution of quinalizarin and 0·25–1·0 ml. of a buffer solution of pH 5·6. Warm to 50° and stand for thirty minutes. The colour given is compared with standards similarly prepared. The best range for comparison is from 0·02–0·5 mg. Al.

Detection of Borate

If a substance suspected of being a borate is dissolved in sulphuric acid (9 vols. acid : 1 vol. water) and a solution of quinalizarin in the same strength sulphuric acid be added, a blue colour is produced as a positive test.

Substances yielding colours with the acid alone must obviously be absent.

Germanic acid and its salts also yield a blue colour with the reagent in concentrated sulphuric acid solution [17].

Colorimetric Determination of Borate

The standard solutions used are:

A: 0·04 per cent. solution of boric acid in water.

B: 0·01 per cent. solution of quinalizarin in sulphuric acid (9 vols. acid : 1 vol. water).

Transfer 1 ml. of the aqueous test solution to a boiling tube, add 9 ml. of concentrated sulphuric acid, mix, and cool. Add 0·5 ml. of solution B and leave, after stirring, for five minutes. If the colour produced is pure blue, more than 0·04 mg. is present in the 1 ml. taken. In this case, dilute the test solution to such a strength that when 1 ml. is tested a red-violet or blue-violet colour results. This colour is matched against standards obtained by treating solution A in the same manner.

If left corked overnight the standard colours develop slightly.

The method will estimate accurately at least two parts of H_3BO_3 in 1,000,000 parts of solution.

Detection of Gallium and Germanium

Full details for the detection of gallium [25] and germanium [18] will be found in the literature.

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RUBEANIC ACID

(Dithio-Oxamide)

$NH_2 \cdot CS \cdot CS \cdot NH_2$

Mol. Wt. 120·2

Reagent for Copper, Cobalt and Nickel

Rubeanic acid is a red crystalline compound, which decomposes at about 200° and has no definite melting-point. It is soluble in alcohol and a saturated solution in this solvent, containing approximately 0·5 per cent. rubeanic acid, is used in the detection and colorimetric determination of copper.

Detection of Copper

To 10 ml. of the neutralised solution are added 1 ml. of acetic acid (5N) and a few drops of the reagent solution. Copper if present produces a greenish-black precipitate or (in great dilution) a dull green colour. One part of copper in 1,000,000 parts of solution can be detected in this way. Nickel and cobalt also give precipitates but by adjustment of the pH of the test solution to about 3·5 with a mixture of sodium acetate and acid, copper only is precipitated. The nickel compound is purple and the cobalt compound is brown. Silver and mercurous mercury give black precipitates but mercuric, lead, cadmium, arsenic, arsenious, stannous, bismuth, aluminium, thallous, ferric, chromic, ferrous, zinc and manganous ions have no effect.

Detection of Copper by the Spot-reaction

A drop of the solution to be tested is allowed to fall on a filter paper and the spot is held over an open bottle of ammonia. A drop of the reagent solution is then placed on the spot and if copper is present a dark greenish spot appears. One part of copper can be detected in 200,000 parts of solution by this method.

An elaboration of this technique has been described by Feigl [3, 4]. The solution containing copper in the presence of nickel or cobalt, acidified with acetic acid, is allowed to fall in a spot upon paper previously soaked in the reagent solution. The characteristic copper spot appears in the centre and, at the edges, where the acidity has become less by diffusion, the colour due to the interfering metal appears. This method has been termed ‘ capillary separation ’.

Determination of Copper

A colorimetric method for the determination of copper may be developed by the analyst but since individual cases require special precautions no general method can be outlined. The following points require attention.

The composition of the comparison solutions should be approximately the same as that of the test and the pH should be in each case the same.

The copper should not be present in amounts great enough to cause a precipitate. The limiting concentration is dependent upon the composition and pH of the solution. *See also* [5, 6].

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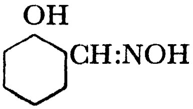
SALICYLALDOXIME



Mol. Wt. 137·1

Reagent for Copper and Nickel

Salicylaldoxime is a white or faintly buff crystalline powder which melts at 57°, and is very soluble in alcohol. The reagent solution is prepared by dissolving 1 g. of the solid in 5 ml. of alcohol and diluting to 100 ml. with water. This reagent when added to a slightly acid solution of a copper salt produces a greyish precipitate or, in great dilution, an opalescence. The complex has the formula $(C_7H_6O_2N)_2Cu$. Silver, mercuric, cadmium, arsenious, ferric, cobalt, nickel and zinc ions do not interfere with the reaction provided sufficient acetic acid is present. The only metals which give precipitates in acid solution are gold, osmium, palladium and vanadium [24]. In ammoniacal solution the reagent has been employed for the gravimetric determination of zinc [20, 25], bismuth [25], lead [27], and nickel [9].

Detection of Copper

The solution to be tested is neutralised and is then rendered acid by means of acetic acid. One twentieth of its volume of the reagent solution is then added. An immediate precipitate or turbidity occurs in the presence of copper, but the opalescence due to a very small trace may take several minutes to develop.

A precipitate is produced at a concentration of 1 in 20,000 and an opalescence can be detected at 1 in 2,000,000.

Detection of Nickel [9]

The solution to be tested is adjusted to pH 7 to 8 and salicylaldoxime solution added. A green flocculent precipitate is produced in the presence of much nickel whilst traces give an opalescence. A faint opalescence is given by one part of nickel in 4,000,000 parts of solution.

Determination of Copper

To the solution containing not more than 0·1 g. of copper, sodium hydroxide solution is added to produce a precipitate. The mixture is then acidified with acetic acid and 50 ml. of the oxime solution are added at the ordinary temperature. The solution is stirred to coagulate the precipitate and is then filtered into a previously tared sintered glass crucible, porosity 4. After washing with cold water until the washings no longer give a brownish purple colour with ferric chloride solution, the crucible is dried to constant weight at 100° to 105°.

$$\text{Wt. of precipitate} \times 0{\cdot}1894 = \text{Wt. of Cu.}$$

Instead of drying the precipitate to constant weight it can be determined by a volumetric procedure as follows [18]. The copper salicylaldoxime complex is dissolved in sulphuric acid to hydrolyse the salicylaldoxime, and the resulting hydroxylamine determined volumetrically. The hydroxylamine is determined by adding excess ferric sulphate and titrating the resulting ferrous sulphate with standard potassium permanganate. The details of the method are identical with those given for the titration of nickel-dimethylglyoxime (p. 43).

$$1 \text{ ml. N/10 potassium permanganate} = 0{\cdot}001589 \text{ g. Cu.}$$

A micro-method is described [4] and also a method for the determination of copper in the presence of iron [7].

Separation and Determination of Copper and Nickel [9]

The solution containing nickel and copper is rendered acid by the addition of 1 g. sodium acetate and 10 ml. glacial acetic acid per 100 ml. of solution, and enough salicylaldoxime solution is added to precipitate both metals. The copper compound separates, and after stirring to coagulate the precipitate, it is filtered on a tared

No. 4 sintered glass crucible and washed with cold water. The compound is dried at 100° and weighed.

Wt. of precipitate × 0·1894 = Wt. of Cu.

To the filtrate and washings ammonia solution is added until the mixture has a pH of 7 to 8. The precipitate is stirred to effect coagulation and then filtered, washed and dried at 100° in the same way as described for copper.

Wt. of precipitate × 0·1774 = Wt. of Ni.

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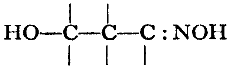

$$\mathrm{HO{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\underset{|}{C}:NOH}$$

Ber., **64**, 1210 (1931). *See also Ber.*, **64**, 2819 (1931).
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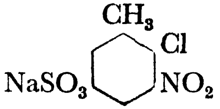
SODIUM 2-CHLORO-3-NITROTOLUENE-5-SULPHONATE



Mol. Wt. 273·6

Reagent for Potassium

Sodium 2-chloro-3-nitrotoluene-5-sulphonate is an almost white or slightly yellow crystalline powder, fairly soluble in water. It finds application as a convenient reagent for potassium—particularly for the quantitative estimation of this element. The solubility of the alkali salts of 2-chloro-3-nitrotoluene-5-sulphonic acid are given as follows (in grams of salt per 100 g. of water):

Temperature	Potassium	Ammonium	Sodium
0°	0·235	0·935	10·4
20°	0·405	1·77	15·05

As regards the salts of the acid with other metals, figures for the solubilities are not available; a qualitative statement may, however, be made as follows.

The barium salt is sparingly soluble and has been recommended as a microchemical test [2], but the salts of silver, lead, copper, cadmium, aluminium, chromium, ferrous iron, ferric iron, nickel, cobalt, manganese, zinc, calcium and strontium are readily soluble and no precipitate is produced when a solution of sodium chloronitrotoluenesulphonate is mixed with moderate concentrations of salts of this group of metals. In their presence, however, the characteristic precipitate with potassium is readily produced, and hence it would appear that the reagent may be used to detect and estimate potassium in the presence of all the common metals with the exception of ammonium and barium.

Detection of Potassium

5 ml. of a 10 per cent. aqueous solution of the reagent are added to 20 ml. of the solution to be tested. In the presence of a considerable amount of potassium, a crystalline precipitate commences to

form immediately; near the limit of sensitivity it is desirable to add a small seed-crystal of the potassium salt. Under these conditions, the results are as follows:

Concentration of K	Effect
1 in 1000	a precipitate immediately.
1 in 2000	a slight precipitate in fifteen minutes.
1 in 2500	a slight precipitate in one hour.

The sensitivity of the test may therefore be given as 1 in 2500.

For purposes of comparison, the sensitivities of other tests for potassium may be given. They are as follows (when carried out in similar manner to the above test):

Perchloric acid (without alcohol)	about 1 in 500
Sodium cobaltinitrite	about 1 in 5000

It was established that the sensitivity of the chloronitrotoluenesulphonate test for potassium remains entirely unchanged when carried out in a 1 in 100 solution of sodium.

Determination of Potassium

The limitations as regards other metals have been dealt with above. Barium must not be present, and any ammonia must be removed by boiling with sodium hydroxide. The determination may be effected in strongly alkaline, neutral, or weakly mineral acid solution; in concentrated mineral acids the potassium salt is moderately soluble.

The solution may conveniently contain about 0·1 to 0·2 g. of potassium in 10 ml., and the reagent is employed in the form of a 10 per cent. aqueous solution. The reagent solution is added in 50 to 100 per cent. excess to the cold solution of the potassium salt (0·1 g. K requires theoretically 7 ml. of the reagent solution for complete precipitation), then the whole is heated to boiling-point. Conditions should be such that the precipitate of potassium salt is just completely dissolved at the boiling-point; if necessary, water should be evaporated, or added, to realise this. The whole is then left overnight at a low temperature (5° or less; if kept at 15°–25° the results are a little low) and filtered on a tared sintered glass crucible (porosity 3), a saturated aqueous solution of the potassium salt being used to transfer the precipitate to the crucible and to wash it. Finally the precipitate is rinsed with a few ml. of cold water and dried to constant weight at 120°.

Wt. of precipitate × 0·135 = Wt. of K.

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SODIUM DIETHYLDITHIOCARBAMATE

$N(C_2H_5)_2{\cdot}CS_2Na$

Mol. Wt. 171

Reagent for Copper and Zinc

This reagent is a white crystalline compound readily soluble in water. The solution employed in analysis (0·1 per cent. in water) undergoes slow decomposition but is quite usable several weeks after preparation.

The substance forms insoluble compounds with a number of metals but is of particular usefulness in the detection and colorimetric estimation of copper. In the presence of this metal, even in minute amounts, a golden brown colour is produced in either acid, ammoniacal or neutral solution. Cyanide inhibits the reaction with copper.

Certain other metals in low concentration give rise to white turbidities, viz., silver, lead, mercury, cadmium, antimony, tin, aluminium, zinc (arsenious ions react in acid solution only), whilst the following metals give rise to coloured compounds—bismuth, iron, manganese, nickel and cobalt. Chromium, unless present in very low concentration, gives rise to a faint turbidity.

The commonly occurring metals iron and lead may easily be removed, the former by precipitation with ammonia and the latter by adding a solution of an iron salt and precipitation with ammonia from the boiling solution, the lead being carried down with the ferric hydroxide. In quantitative work it is not recommended to separate iron by precipitation with ammonia since it has been shown that the ferric hydroxide carries down a proportion of the copper [5].* The reaction of iron with the diethyldithiocarbamate may, however, be prevented by the addition of citric acid, and this principle is adopted in the colorimetric technique described below.

Zinc does not interfere if the test for copper is carried out in presence of ammonia in sufficient concentration, since the zinc compound is not precipitated under these conditions. Barium, calcium, strontium, magnesium, and the alkali metals do not interfere.

The copper compound has a very low solubility in water, but dissolves to a greater extent in certain organic liquids and may be completely extracted from water by one or other of these solvents. Such extractions offer a threefold advantage. A clear, coloured solution is obtained as distinct from the brown turbidity which is produced in aqueous media. The extraction results in a concentration of the colour and extends the useful range of the reagent for colorimetric purposes. The copper compound may also, by this means, be separated from other coloured compounds which may occur in the sample under examination. Three organic liquids have been proposed for this purpose,—amyl alcohol, chloroform and carbon tetrachloride. Amyl alcohol has the disadvantage that it does not readily separate from the aqueous layer; it is also rather soluble, and is not conveniently separated since it forms the upper layer. Carbon tetrachloride is almost insoluble in water, it falls to the bottom of the tap funnel and is readily separated. Although the tetrachloride does not dissolve the copper compound quite so readily as chloroform it has generally been found the most convenient of the three in use.

Detection of Copper

The solution, which must not contain any of the above metals in quantity sufficient to mask the reaction, is rendered ammoniacal and about one tenth its volume of a 0·1 per cent. solution of sodium diethyldithiocarbamate in water is added. The sensitivity of the reaction is such that 0·001 mg. of Cu may be detected in 100 ml. of water (one part in 100 millions).

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* A more recent paper [11] shows that if sufficient ammonium salts and ammonia are present adsorption is inhibited.

Colorimetric Determination of Copper

The colour produced by the unknown quantity of copper is compared with that produced by measured quantities of a standard solution of copper containing 0·01 mg. Cu per ml. (0·0393 g. $CuSO_4 \cdot 5H_2O$ per litre). The two solutions are placed in similar Nessler glasses of 100 ml. capacity and are both rendered slightly ammoniacal, 10 ml. of a 0·1 per cent. solution of the reagent in water are then added and the solutions made up to the 100 ml. mark with water. Quantities of copper exceeding 0·1 mg. give colours too deep for accurate comparison and in such cases an aliquot portion should be taken.

Should it be found desirable to extract the colour, the solution is shaken with successive 3–5 ml. portions of carbon tetrachloride until no more colour is extracted. Comparison standards are prepared in the same manner.

When iron is present this metal is oxidised to the ferric condition. 2 g. of citric acid are added, the solution made more alkaline than pH 9 with ammonia and the copper determination carried out as described above, extracting with carbon tetrachloride.

The use of gum tragacanth or gelatine has been recommended [10]. The protective action of these colloids prevents precipitation of the coloured copper compound from aqueous solutions and enables the analyst to deal colorimetrically with amounts of copper which would otherwise require extraction.

Estimation of Minute Quantities of Zinc

The reagent used is a 0·1 per cent. solution of sodium diethyldithiocarbamate in water. To 50 ml. of the neutral aqueous solution (copper free) are added 5 ml. of the reagent. Any turbidity produced is matched against a zinc sulphate standard which is submitted to the same conditions.

The reagent has found particular application to the determination of zinc in water [15, 19, 37].

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TANNIC ACID

$C_{14}H_{10}O_9$

Mol. Wt. 322·1

Reagent for Titanium, Vanadium, Molybdenum, Iron, Tungsten and other metals

The reagent solution is a 10 per cent. aqueous solution, which should be freshly prepared.

Detection of Titanium

About 15 ml. of the test solution are acidified with acetic acid, the whole boiled and 1 ml. of reagent solution added. If titanium is present a red-orange colour is given which in some metallic combinations is adsorbed upon a precipitate. This test will easily detect titanium in a concentration of one part in 10,000,000 parts of solution. Titanium may be detected in presence of 1000 times as much bismuth, beryllium, tin, uranium, antimony, magnesium, calcium, strontium, potassium, sodium, barium, zinc, cadmium, aluminium, thallium, lead, mercury, silver and arsenic. Molybdenum and vanadium interfere giving red and blue precipitates respectively.

Detection of Vanadium

Tannic acid with a neutral or acetic acid solution of a vanadate yields a dark blue precipitate which in small concentration resolves into a coloration. The coloration produced serves to detect vanadium in a concentration of one part in 10,000,000, and vanadium may be detected in the presence of 1000 times as much bismuth, beryllium, barium, strontium, calcium, magnesium, zinc, cadmium, aluminium, arsenic, antimony, mercury, tin, lead, silver and uranium. Molybdenum and titanium interfere, giving their characteristic colours.

Detection of Molybdenum

With neutral molybdates, tannic acid gives a red precipitate or coloration, serving for its detection. The test detects molybdenum in a concentration of one part in 10,000,000 parts of solution and will detect molybdenum in the presence of 1000 times as much bismuth, beryllium, uranium, magnesium, calcium, barium, strontium, zinc, cadmium, aluminium, thallium (on boiling) and arsenic. Similar excesses of tin, antimony, lead, mercury, silver, iron, vanadium and titanium interfere.

Detection of Iron

A neutral iron solution gives with tannic acid a blue precipitate which turns red on the addition of excess ammonia. In the absence of heavy metals in excess, iron may be detected in a concentration of two part per million of solution, this concentration giving a pink coloration.

Determination of Titanium

Titanium may be precipitated from acetate solution by means of tannin, although a double precipitation is advised in order to obtain pure TiO_2 on ignition.

The neutral solution containing approximately 0·1 g. Ti is diluted to 250 ml., 10 g. ammonium acetate, and 20 g. ammonium nitrate are added, followed by 25 ml. of glacial acetic acid. The solution is boiled and 10 ml. of 10 per cent. tannic acid solution are added with stirring. After ten minutes boiling, the red-brown precipitate is filtered at the pump, using slight suction. After the filtration, the filter paper and precipitate are transferred to the original beaker and the titanium complex dissolved in 20 ml. of 5N nitric acid by heating, which also macerates the filter paper. The solution is now neutralised to litmus by means of ammonia and the same procedure followed in the second precipitation.

The precipitate is dried in the oven, and ignited with filter paper to TiO_2 which contains 59·95 per cent. of Ti.

By this method titanium may be quantitatively separated from uranium and beryllium.

Determination of Tungstate

The tungstate solution containing some sodium chloride is diluted to 150 ml. and adjusted to the colourless point of phenolphthalein. A fresh solution of 0·5 g. of tannin in 20 ml. of water is added, followed by dilute hydrochloric acid until the solution is acid to litmus. Boiling is effected and carried on for five minutes when 5 ml. of 5 per cent. cinchonine hydrochloride solution are added followed by five minutes more boiling. After leaving overnight the precipitate is filtered and washed with 5 per cent. ammonium chloride (containing a little tannic acid).

The filter paper and precipitate are dried and ignited to WO_3.

In place of cinchonine, the collecting agent used by Schoeller and Jahn, Moser and Blaustein recommend antipyrine. By this process separations from aluminium, iron and chromium are claimed, using double precipitations.

Detection of Barium, Strontium and Calcium

To the neutral test solution add an equal volume of a 0·1 per cent. aqueous solution of tannic acid followed by a little decinormal caustic soda. The presence of the alkaline earth metals is indicated by development of a blue or green colour.

A positive reaction is given by each of the three metals in concentrations greater than one part in 100,000 parts of solution. Small amounts of either zinc or magnesium do not interfere.

Detection of Cerium [53]

With tannic acid in 50 per cent. glycerol solution cerium gives a blue-violet colour. The reaction is stated to be specific and to detect 8 gamma of the metal.

Other Metallic Separations

By the use of tannin in mineral acid solution, niobium and tantalum may be separated from titanium, zirconium and vanadium.

Using antipyrine as collecting agent, titanium may be precipitated from solutions containing iron, aluminium, chromium, nickel, cobalt, zinc, manganese or phosphate although the determination of these radicals in the filtrate is difficult as antipyrine cannot be destroyed by wet methods [27].

In acetate solution, aluminium may be separated from beryllium [10, 30], and the latter may be freed from iron, chromium, thorium, vanadium, titanium and zirconium [11], and also tin [21]. The separation of iron from beryllium has, however, been criticised by Dixon, since uranium interferes. In acetate solution also, gallium may be separated from zinc, nickel, cobalt, manganese, cadmium, beryllium and thorium [22]. A method for the precipitation of copper from an acetate solution has been described [6, 36].

Tungsten may be separated from aluminium, titanium, tantalum, niobium, zirconium and thorium [18], uranium and vanadium [34, 45], and gallium [22], by the use of tannin in tartrate solutions.

From salicylate solutions, separation of titanium from niobium and tantalum is claimed [16, 31], the two latter being microdetectable, as are titanium, molybdenum and vanadium, in oxalate solution.

Gravimetric estimations of manganese [38], beryllium [42], and the rare earths [41], in ammoniacal tartrate solution are also described in the literature given below.

One of the most important uses of tannin is for the separation of niobium and tantalum, perfected by Schoeller and his coworkers after many years' work [33, 48].

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THIOGLYCOLLIC ACID

(Mercapto-acetic acid, Thiolacetic acid)

$HS \cdot CH_2 \cdot COOH$

Mol. Wt. 92·1

Reagent for Iron

Thioglycollic acid is a colourless liquid, with a strong, unpleasant characteristic odour, freely miscible with water. It boils at about 105° at 15 mm. pressure, and is converted by oxidising agents into dithiodiglycollic acid $S_2(CH_2 \cdot COOH)_2$.

The compound is employed as a reagent for iron in ammoniacal solution, when a pink or reddish-purple colour, according to the amount of iron present, is produced. Under these conditions, the following elements may interfere, the colours produced being given in each case: cobalt, brownish yellow, nickel, brownish red, manganese, green, quickly fading, and uranium, yellow. The following metals do not interfere with the qualitative detection of iron, even when present in considerable amount: silver, lead, mercury, copper, cadmium, aluminium, chromium, zinc, barium, strontium, calcium, magnesium, potassium and sodium.

Detection of Iron [1, 2]

To 10 ml. of the solution to be tested, which should be neutral or slightly acid, and free from oxidising agents, two drops of thioglycollic acid are added, followed by sufficient ammonia to render the whole distinctly alkaline. The quantity of ammonia is not at all critical. In the presence of iron, a pink or reddish-purple colour is at once produced, according to the amount of iron present. The sensitivity is about one part of iron in 5,000,000 parts of water, which is the same as that of the thiocyanate reaction for iron.

The colour is fairly stable, but fades after a time, due to oxidation of the thioglycollic acid by the atmosphere. It can be restored by the addition of more thioglycollic acid. Strong bases readily discharge the colour, whilst ammonia, even in considerable excess, has but little effect. The state of oxidation of the iron is immaterial.

Determination of Iron [2]

The pink colour produced with thioglycollic acid in the solution to be tested is matched in the colorimeter against solutions containing known amounts of iron. It is convenient to adjust the concentration of iron in the solutions to about 1 in 500,000. This gives the total iron present in the solution. If it is required to ascertain the proportion of iron present in the ferrous and ferric conditions, a fresh portion of the unknown solution should be treated with hydrochloric acid and thiocyanate, and compared colorimetrically against standard solutions of ferric iron. Thus the ferric iron is ascertained and the ferrous iron is obtained at once by difference.

The determination of iron with thioglycollic acid is remarkably free from interference by the common anions [10]. Thus fluoride, iodide, nitrate, orthophosphate, pyrophosphate, sulphate, chlorate, tartrate, oxalate, citrate, acetate, bromide, thiocyanate, sulphite, chloride and borate can be present in large excess and cause no variation in the iron colour. Cyanide and nitrite, however, interfere with the test and must be absent. A number of metals interfere with the determination of iron, e.g., nickel, cobalt, copper, etc., but a more serious fault is the use of an alkaline solution which precipitates many metals, thereby making colorimetric comparisons difficult [10].

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THIOUREA

$H_2N \cdot CS \cdot NH_2$

Mol. Wt. 76·2

Reagent for Bismuth, Lead, Thallium, Osmium and Ruthenium

A white crystalline substance melting at 182°, the reagent is appreciably soluble in water, and a 10 per cent. aqueous solution is used in the qualitative detection of bismuth.

Detection of Bismuth

To the test solution (0·5–1N in respect of HNO_3) is added one tenth of its volume of reagent solution. In a concentration of one part Bi per 1,000,000 parts of solution a yellow colour is just visible.

By this method bismuth may easily be detected in presence of 10,000 times as much zinc, manganese or magnesium, and 5000 times as much lead, calcium, barium, strontium, cadmium, arsenic, aluminium, ferrous iron, and tin (using just enough hydrochloric acid to maintain solution in the latter case).

Silver, mercury and antimony precipitate with the reagent, but the precipitates are easily soluble in excess reagent solution. Interference may thus be removed by the use of a larger volume of reagent, excepting the case of antimony, which itself yields a pale yellow colour with thiourea. This colour, however, may be appreciably suppressed by the addition of a fluoride.

Determination of Bismuth

To 10 ml. test solution (0·8N in respect of HNO_3) add 1 g. thiourea and filter if necessary. Wash the filter with a saturated solution of thiourea in 0·8N nitric acid, and dilute the combined filtrates to 25 ml. with the latter solution. Match the yellow colour given against standards similarly prepared. Quantities of bismuth from 0·05 to 1·0 mg. constitute the best range for matching.

Quantitative Separation of Lead

By saturating acid lead solutions, containing nitrate, with thiourea, practically insoluble lead thiourea nitrate $2Pb(NO_3)_2 \cdot 11CS(NH_2)_2$ is precipitated. Almost all other metals give soluble thiourea complexes or soluble nitrates and remain in solution.

No interference is given by silver, mercury(ic), copper, bismuth, cadmium, arsenic, antimony, tin, cobalt, nickel, iron(ous), manganese, aluminium, chromium, zinc, barium, strontium, calcium, zirconium, beryllium, uranium, or thorium.

Ferric iron should be reduced by boiling with hydrazine sulphate and chromate by boiling with alcohol.

Thallium reacts similarly to lead.

Details of the separation are as follows:—

Dilute the nitric acid test solution with water until it is 1–2N with respect to HNO_3. An equal volume of freshly prepared thiourea solution (about N/1 with respect to HNO_3 and saturated at 25–30°) is added and the whole cooled to 0° in ice.

Add solid thiourea until the whole solution is saturated with it (when the kernels of thiourea can be seen mixed with the lead precipitate). Stand for thirty minutes at 0°, and filter through a sintered crucible. Wash with ice-cold reagent solution (as used above), suck dry, empty and clean the receiver.

Wash the precipitate through with warm water and rinse the filter thoroughly with cold water. To the combined filtrates add ammonium acetate and precipitate in the usual way with chromate or dichromate solution.

Roast the filtered lead chromate precipitate at 550–600° to constant weight.

It should be noted that some metals, such as silver and copper, give a precipitate on first adding the acid reagent solution. This, however, will redissolve on further addition of reagent solution.

Quantitative Separation of Thallium

It is reported [22] that mono or trivalent thallium can be separated from mercury, silver, copper, cadmium, iron, manganese, nickel, cobalt, chromium, aluminium, zinc, barium, strontium or calcium in one precipitation by means of thiourea in dilute perchloric acid solution.

When lead is present a double precipitation is required, and in presence of both lead and silver, nitrate must be removed by evaporation with perchloric acid.

The precipitation is carried out by treating the test solution, containing 2 per cent of $HClO_4$, with an equal volume of 10 per cent. aqueous solution of thiourea. After cooling in running water for thirty minutes the precipitate of $TlClO_4 \cdot 4CS(NH_2)_2$ is filtered off, and washed with a 5 per cent. aqueous solution of thiourea containing a little perchloric acid.

The precipitate is dissolved in ammonia and reprecipitated as $TlCrO_4$ or alternatively treated with excess bromine and determined volumetrically with iodide and thiosulphate.

In the absence of lead or silver, thallium may be separated as $TlNO_3 \cdot 4CS(NH_2)_2$ by a method similar to that already given for lead.

Detection of other elements

When ruthenium and osmium, present as chlorides, are heated for a short time with thiourea and hydrochloric acid (s.g. 1·18), blue and red colours, respectively, are given, best if the reactions are carried out in presence of stannous chloride [11].

Gilchrist [8] obtained a sensitivity for osmium of 1 part in 5 millions by this reaction.

Thiourea, used in conjunction with Reinecke's salt, has been employed for the quantitative precipitation of cadmium and its separation from zinc [14].

When an aqueous solution of thiourea is added to a neutral solution of a tellurite, a white precipitate is thrown down, easily soluble in dilute hydrochloric acid. When this acid solution is boiled a black precipitate is produced. The test in this form may be made very sensitive for tellurites.

Under the same conditions, selenites yield a ruby-red colloidal precipitate, also a very delicate test.

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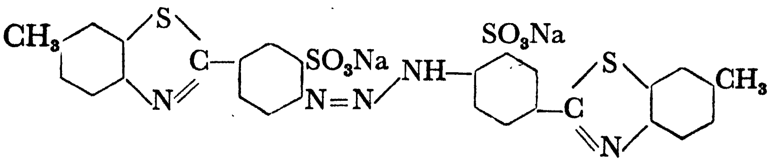
TITAN YELLOW

(Clayton Yellow)



Mol. Wt. 695

Reagent for Magnesium

Titan yellow is an orange-red solid which dissolves in water to give a yellow solution. In alkaline magnesium solutions a red coloration is given which serves to detect magnesium in a concentration of one part in 3,000,000 parts of solution.

Detection of Magnesium

The test, which is conveniently done in Nessler cylinders, is carried out by adding three drops of a 0·1 per cent. aqueous reagent solution to the test solution (neutral or slightly acid), followed by excess of normal potassium hydroxide.

The test will detect magnesium in one thousand times as much barium, strontium, calcium, and in presence of potassium cyanide, zinc, mercury, cadmium, lead, beryllium, and copper. The following metals in similar excess cause interference:—tin, aluminium, arsenic, bismuth and manganese. If cobalt or nickel is present in excess, unavoidable colour interference is encountered.

Determination of Magnesium

In the absence of barium and calcium, which intensify the reaction, and interfering metals, the magnesium content may be estimated by comparing the colour given with standards made under the same conditions, best in presence of a protective colloid [16].

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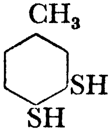
TOLUENE-3 : 4-DITHIOL

‘ Dithiol ’

(4-Methyl-1 : 2-dimercaptobenzene)



Mol. Wt. 156

Reagent for Tin

Toluene-3:4-dithiol is a white crystalline solid melting at 31°, which tends to liquefy on exposure to air. The ortho-dithiols form insoluble mercaptides with a number of metals and these mercaptides are for the most part highly coloured. The complexes formed with toluene-3:4-dithiol and silver, mercury, cadmium, arsenic, antimony and lead are all varying shades of yellow; copper, nickel and cobalt yield black precipitates while tin and bismuth give rise to magenta red and brick red precipitates respectively. The molybdenum, tungsten, rhenium and palladium complexes have also been described, the first three are green, while the palladium compound is dark brown.

The reagent solution is prepared by dissolving 0·2 g. toluene-3:4-dithiol in 100 ml. of 1 per cent. sodium hydroxide solution and adding about 0·3 g. thioglycollic acid. The use of thioglycollic acid in the reagent solution is not imperative but it serves to facilitate the reduction of stannic tin to the bivalent state.

Detection of Tin [1]

The test is best applied by adding a few drops of the reagent solution to an acid solution, containing up to 15 per cent. hydrochloric acid, of the tin salt and warming the mixture, when a red colour or precipitate appears. In this way one part of tin per 1,000,000 parts of solution can be detected. Metals, with the exception of lead, which give coloured precipitates with the reagent interfere with this test. Nitrites must be absent as they give a red colour with thioglycollic acid, phosphates cause a diminution of the sensitivity and nitric acid below 1 per cent. does not interfere but on prolonged boiling decomposes the tin complex. Organic acids do not affect the test but organic substances of a colloidal nature, e.g., starch, interfere seriously.

Colorimetric Determination of Tin [3]

For the colorimetric determination of tin 1 ml. of a stiff agar-agar jelly, 2 ml. of the reagent solution and 1 ml. concentrated hydrochloric acid are added to the solution under test and the volume made up to 10 ml. The solution is heated by immersion in boiling water for one minute. The colour is compared with those given by standard tin solutions. The agar-agar serves to prevent coagulation of the precipitate.

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URANYL ZINC ACETATE AND URANYL NICKEL ACETATE

Reagents for Sodium

Mixtures of uranyl acetate solution with the acetates of zinc, magnesium, cobalt, nickel or manganese have been used to detect and determine sodium. There are many recommended formulæ for the reagent solution and many techniques, but the double acetates of zinc and nickel only are described in this monograph. These two reagents, made according to the directions of Kolthoff [1, 2, 4, 7] and Feldstein and Ward [50] respectively, are more sensitive than the other reagents which have been described. Certain of these latter contain alcohol, which appears to reduce the uranium solution in a few days and which has been said to affect the specificity of the method [74]. Bibliographies are appended referring to all the double acetates and also to the use of uranyl acetate in the detection of sodium.

When uranyl zinc acetate solution is added to a neutral solution of a sodium salt, a yellow crystalline precipitate of sodium zinc uranyl acetate $NaZn(UO_2)_3(C_2H_3O_2)_9{\cdot}6H_2O$ appears. The triple acetate is slightly soluble in water, but insoluble in the precipitant, in alcohol and in ether.

Uranyl nickel acetate produces a similar precipitate $NaNi(UO_2)_3(C_2H_3O_2)_9{\cdot}6H_2O$ of yellowish-green colour.

Strict adherence to the conditions described below is necessary to ensure accurate quantitative results.

Preparation of a solution of uranyl zinc acetate

The following two solutions are made with the aid of heat:

(*a*)	Uranyl acetate	10 g.
	Acetic acid (30 per cent)	6 g.
	Water to	65 g.
(*b*)	Zinc acetate	30 g.
	Acetic acid (30 per cent.)	3 g.
	Water to	65 g.

When the solids have dissolved the solutions are mixed, allowed to cool to 20° ± 1° and kept at this temperature for several hours. The solution is then filtered from the triple salt which crystallises, and may be assumed to be saturated with regard to sodium at 20°, since the reagents usually contain sufficient sodium to give a precipitate of the triple acetate.

Preparation of a solution of uranyl nickel acetate

The following solution is made with the aid of heat:

Uranyl acetate	14 g.
Nickel acetate	40 g.
Acetic acid (glacial)	12 ml.
Water to	200 ml.

The solution is allowed to cool to 20° ± 1° and filtered after keeping at this temperature for several hours. The resulting solution may be assumed to be saturated with the sodium triple salt for the reasons described under the preparation of the zinc solution.

Detection of Sodium

The solution to be tested is neutralised and an equal volume of the reagent solution is added at 20°. In the presence of sodium a yellow crystalline precipitate of the triple acetate is deposited, when the zinc compound is used. If the nickel compound is used the crystals are of a bright yellowish-green colour. At high dilutions the precipitate may not appear until fifteen to twenty minutes have elapsed and scratching with a glass rod may be necessary to initiate precipitation. One part of sodium in 2000 parts of solution can be detected in this way.

Attention has been drawn to the possibility of the volume of water present in the solution under test being sufficient to dilute the reagent and render it capable of dissolving the small amount of triple salt formed [77]. On the other hand, if the volume of test solution is very small the reagent may precipitate sodium uranyl acetate instead of the triple compound.

Magnesium, cobalt and manganese uranyl acetates have also been used to detect sodium, and uranyl acetate also has found application as a micro-reagent for the same purpose. (See bibliography.)

The method has been applied in the presence of potassium, magnesium, barium and calcium which have no effect. By the adoption of a modified technique, sodium can be detected in the presence of strontium, lithium, rubidium, cæsium, phosphates and arsenates [7].

Potassium in high concentration produces a precipitate of needle-shaped crystals and inhibits the formation of the characteristic octahedral sodium triple acetate to a very slight extent. Thus a microscopic examination of the precipitate produced by the reagent and a potassium salt serves to show the presence of sodium in the latter.

Determination of Sodium

(*a*) *Gravimetric.*—To 1·0 ml. of the neutral solution, containing not more than 0·008 g. of sodium, 10 ml. of the reagent is added and the mixture allowed to stand at $20° \pm 1°$ for thirty to forty-five minutes with occasional stirring. The crystals are then filtered on a tared sintered glass crucible, porosity 4, and washed with five successive amounts of 2 ml. of reagent, then with five amounts of 2 ml. of alcohol (previously saturated at 20° with the triple acetate), and finally with ether. The precipitate is dried at 40° for ten to fifteen minutes and weighed.

Wt. of precipitate × 0·01502 = Wt. of Na (Nickel compound).
Wt. of precipitate × 0·01495 = Wt. of Na (Zinc compound).

Barium, calcium, magnesium and zinc do not interfere and potassium has little effect if less than 0·05 g. be present. Lithium, phosphates, oxalates and tartrates should be absent [4]. The method can be applied to the determination of sodium in the presence of rubidium, cæsium, potassium, lithium, phosphates or arsenates by observing suitable precautions [7, 51].

(*b*) *Volumetric.*—Instead of weighing the triple acetate it may be titrated by one of the following methods, which are grouped into three classes: reduction and titration of uranous ions, titration of the zinc present, and various precipitation methods. The permanganate titration and the acidimetric method are recommended.

1. The triple salt is dissolved in 2 per cent. sulphuric acid and

reduced in a reductor containing amalgamated zinc. The uranyl compound is thereby reduced to a mixture of $U^{\cdot\cdot\cdot}$ and $U^{\cdot\cdot\cdot\cdot}$ ions. The reduced solution is then stirred for about five minutes by a rapid stream of air, and the resulting solution of uranous salt is titrated with N/10 potassium permanganate solution [12, 19, 56].

1 ml. N/10 potassium permanganate = 0·0003833 g. Na.

The uranous salt may be determined by adding excess of ceric sulphate solution and titrating the excess potentiometrically by means of ferrous iron [68].

Another method is to titrate with potassium dichromate in the presence of phosphoric acid using barium diphenylamine sulphonate and ferric chloride as indicator [22].

Reduction may be effected by means of an excess of titanous chloride and the excess may then be titrated with ferric alum using thiocyanate as indicator [10].

2. An iodometric method has been described [21] which consists in dissolving the precipitate in sulphuric acid, adding ammonium sulphate and potassium iodide and then after adding an excess of potassium ferricyanide, titrating with thiosulphate.

3. The precipitate is boiled with excess of sodium hydroxide solution and the excess is titrated with standard acid at the boiling-point using phenolphthalein as indicator [16].

1 ml. N/10 sodium hydroxide = 0·00023 g. Na.

The uranium in the triple acetate has been titrated by means of standard phosphate solution [18].

(*c*) *Colorimetric.*—The triple acetate precipitate may be dissolved and the colour of the solution matched in a suitable colorimeter against standard solutions of the pure complex salt. Very small amounts are more conveniently matched by adding ferrocyanide to the uranium solutions [3, 15, 17, 24, 76].

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NITRATE REAGENTS

Many phenols may be used as reagents for the detection of nitrate (or nitrite) by virtue of their easy nitration (or nitrosation). These nitro (nitroso) derivatives give intense yellow colorations on making alkaline with sodium hydroxide and in a few cases a nitrate (or nitrite) estimation is possible by comparing the yellow colour given with standards. Phenols having this property which have been investigated in this laboratory are:

1. α-Naphthol-β-sulphonic acid
2. Phloroglucinol
3. Resorcinol
4. Salicylic acid
5. 1·3-Xylen-4-ol
6. Salicylsulphonic acid
7. Pyrogallol
8. Phenoldisulphonic acid

Of these, the most sensitive are 2, 3 and 5, while phloroglucinol and the xylenol may be used for the estimation of nitrates.

Detection and Determination of Nitrate

If phloroglucinol is used, a saturated aqueous solution of the reagent is prepared. To 1 ml. of the test solution add five drops of the saturated reagent solution and 1·5 ml. concentrated sulphuric acid. Leave for five minutes, add 15 ml. of water and excess of 5N sodium hydroxide. The volume is made up to 50 ml. in a Nessler cylinder.

If the colour given is orange, the test solution should be diluted until 1 ml. gives a yellow coloration, since at higher nitrate concentrations the colour given is not strictly proportional.

1·3-Xylen-4-ol is used as a 1 per cent. aqueous solution and in this case the nitro-compound formed may be steam-distilled (with unchanged xylenol) into excess sodium hydroxide. Because of this property, 1·3-xylen-4-ol has been applied to the determination of nitrate in soils and plants [3], and in meat products [5]. For this estimation, 1 ml. of the test solution is diluted with 4 ml. of water; 15 ml. of 60 per cent. *v/v* sulphuric acid are added, the mixture being maintained at 35°, when three drops of the reagent solution are added, and the solution kept for thirty minutes at this temperature. 100 ml. of water are now added and 50 ml. are distilled into a Nessler cylinder containing 5 ml. of 1 per cent. aqueous sodium hydroxide solution. The yellow colour produced is compared with standards made under *identical* conditions.

Yoe [2] has used pyrogallol in a ‘ ring ’ test for nitrate determination. To 10 ml. of the test solution are added five drops of a 2 per cent. aqueous pyrogallol solution. The tip of a pipette is placed under the liquid and 2 ml. of concentrated sulphuric acid are introduced. A small quantity of sodium chloride is added, causing a violet coloured ‘ ring ’ to appear at the acid surface. From the intensity of colour produced, the nitrate concentration may be guessed by an experienced worker. A standard containing this amount is prepared and compared with the test.

Phenol disulphonic acid is commonly employed for the colorimetric determination of nitrate in water and is specific for nitrate in presence of nitrite.

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INTERFERENCE TABLE

The table overleaf will be, we hope, an almost self-explanatory guide to the analyst regarding the necessity of removing a metal when testing for impurities in its mineral salts.

The positive sign indicates that removal is not necessary, the letter R indicating that removal is essential.

All the tests from which this table was compiled were performed with the unreacting metal in one thousandfold excess.

The tests employed are all colorimetric in nature and are purely qualitative in scope.